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The STORY *of* MATTER

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Preface

The Story of Matter has been written to bridge the gap that too frequently occurs between junior matriculation chemistry and college chemistry. This gap develops because matriculation courses tend to emphasize the facts of chemistry, and college courses, the general theories. We believe that facts themselves have little intellectual significance and only limited practical usefulness if the student cannot correlate them and interpret them in the light of general chemical theories. On the other hand, theories are meaningless unless they are used to make facts understandable. It is the aim of this book to present chemical theory in close relationship with practical interpretation.

As far as it was feasible to do so, the authors have grouped the chemical theories under eight topics, each topic being developed and supported by a body of illustrative facts. *Each topic of chemical theory is developed in a logical and uninterrupted sequence and serves to interpret the facts.* This systematic development is based on the historical pattern, which seems to give the arrangement the closest unity, simplicity and cultural value. Each great concept thus emerges as the solution to an important problem in understanding the nature of matter. Regardless of whether theoretical principles precede the factual material, or, (as in Topic 5) the facts lead to the theoretical generalization, or (as in Topic 8) the two are developed together, we feel that we have in large measure accomplished our purpose in making the great principles of chemistry simple, clear, understandable, interesting and significant.

The Story of Matter is designed to develop chemical concepts in the minds of students without undue concern for the memorization of definitions. Definitions are, therefore, integrated with the story but the subject of each definition is indicated by the use of italic type. The understanding of chemical concepts is enhanced by the *question summary* which requires the student to express the essence of each section in his own words. It will be noted that, for easy reference, the number of each question corresponds with the number of the section to which it is related. This will facilitate self-testing, class recitation and review.

Since it is impossible to secure any mastery of scientific principles without learning to apply them to specific problems there are *four chapters devoted mainly to showing step-by-step the method of using the fundamental principles.* Numerical problems are separated from the qualitative questions in order to facilitate the testing of this aspect of learning. The problems are graded so that the student may master one skill at a time and later combine his skills in the solution of more complex problems.

Since the most serious stumbling-block to the learning of chemistry is the mastery of chemical names and formulas, particular attention has been given to arranging *a complete outline of the essential features of chemical nomenclature*, together with the simplest possible set of rules, explanations and illustrations.

In an introductory story even the most elementary concepts should be presented in a manner sufficiently accurate to be capable of extension as learning proceeds. Therefore, in making even a simple drawing or explanation *we have made every effort to keep the latest modern developments in mind.* As a result, we have had to abandon the classical grouping of the elements into A and B families or sub-groups, and to use the modern rational grouping into characteristic elements

(A families) and transition elements (B families). Furthermore, an examination of Canadian High School curricula showed that it would be more convenient for teachers if metals and their compounds were treated in families rather than in chemical or industrial groups. While this method is somewhat more cumbersome, it does make the material adaptable to almost any type of course.

Among the important features of the text the following should be noted:

1. The summarization of important data in the 45 tables and the Appendix.
2. The pairing of illustrations to give them clear effectiveness and significance.
3. The extensive index.
4. The use of chapter and section numbers at the top of pages for convenient reference.

We would welcome any comment on the text, and particularly any suggestions for its improvement or for the correction of errors that may have remained unnoticed.

We are much indebted to the individuals, firms and publishing houses who have so kindly furnished illustrations and to the high school teachers and professors who have criticized the manuscript. The senior author wishes to thank Dr. S. Basterfield for his inspiration and encouragement during the formative stages of the book. We also wish to acknowledge the help and forbearance of our wives and superiors and to thank sincerely all those who have assisted us in any way.

M.R.F. & H.R.C.

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Topic One

THE EARLY WORK

Here you may read the story of matter from the earliest times to the beginning of the modern period. Man's curiosity and ingenuity led him to try to alter matter to suit his needs and chemistry was born. His intelligence led him to seek explanations for physical and chemical changes so chemistry became a science. The earliest chemical science was alchemy which arose in Egypt and was introduced to Europe by the Arabians. Next chemicals were used for the cure of bodily ills and doctors became chemists. They developed methods for collecting gases, purifying liquids, separating solids from liquids and dozens of other chemical techniques until it became possible to make chemistry an exact science. Robert Boyle showed how the scientific method could be used to establish truth and then the nature of fire, water, air and many other substances could be demonstrated.

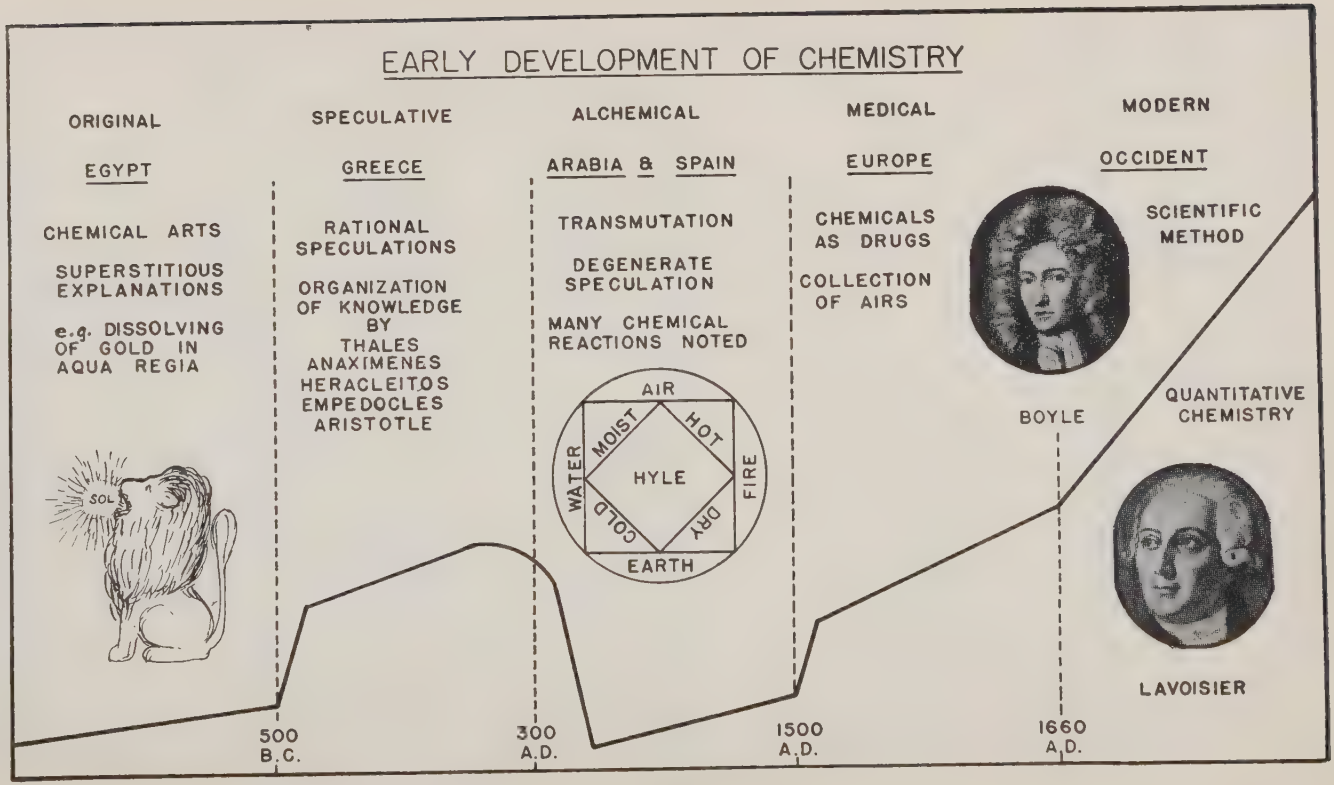

EARLY DEVELOPMENT OF CHEMISTRY
ORIGINAL
EGYPT
CHEMICAL ARTS
SUPERSTITIOUS EXPLANATIONS
e.g. DISSOLVING OF GOLD IN AQUA REGIA
SOL
SPECULATIVE
GREECE
RATIONAL SPECULATIONS
ORGANIZATION OF KNOWLEDGE BY
THALES
ANAXIMENES
HERACLEITOS
EMPEDOCLES
ARISTOTLE
ALCHEMICAL
ARABIA & SPAIN
TRANSMUTATION
DEGENERATE SPECULATION
MANY CHEMICAL REACTIONS NOTED
AIR
HOT
FIRE
DRY
EARTH
COLD
WATER
MOIST
HYLE
MEDICAL
EUROPE
CHEMICALS AS DRUGS
COLLECTION OF AIRS
MODERN
OCCIDENT
SCIENTIFIC METHOD
BOYLE
QUANTITATIVE CHEMISTRY
LAVOISIER
500 B.C.
300 A.D.
1500 A.D.
1660 A.D.

Fig. 1.

Chapter 1

The Scientific Method

1. Introduction. The story of matter is a mystery story. The origins of matter are clouded in mystery and the ultimate nature of matter is enveloped in the shroud of minuteness. The hero of the story is the inquisitive mind of man. The heroine is the instinct to understand. The locale of the story swings in a great arc around the eastern end of the Mediterranean and across the northern shore. From there it spreads northward and finally to the east and the west until it envelops the continent of Europe and the Americas, the British Commonwealth of Nations, and reaches into the Far East.

In order to aid you in visualizing how man slowly realized a few differences in the forms, operations and behaviourisms of matter the topic chart has been prepared to summarize the stages in this development (see Fig. 1).

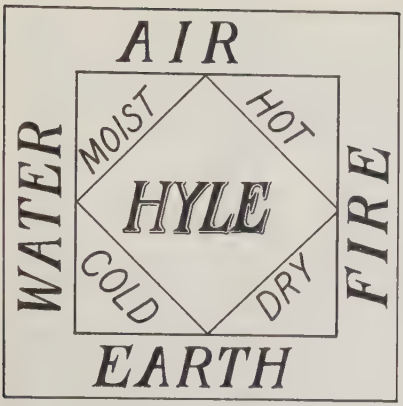
2. Early Chemistry. Modern scientific chemistry dates from the time when Robert Boyle enunciated the scientific method but man's use of chemical changes dates back several thousand years. The peoples of ancient Greece, Rome, China, Egypt and Arabia had a good deal of knowledge about copper, silver, gold, tin, lead, iron and mercury. They knew how to prepare medicines, dyes, beverages, vinegar, pottery and glass but they did not understand the nature of the changes involved in these processes.

The Greeks introduced speculative ideas about the nature of matter and the idea of fundamental elements such as fire, water, air and earth. They also conceived the idea

that matter was made of invisibly small particles but all proof of such reasoning was prevented by a lack of experimental evidence.

Fig. 2. The alchemist at work in his laboratory.

3. Alchemy. Aristotle propounded the idea that all forms of matter were made from a basic substance called "hyle" and it should be possible to transmute one substance into another. All the efforts of the learned men after the decline of the Greeks were devoted to the task of transforming the cheap (base) metals into the precious (noble) metals. This period is called *alchemy* and it produced many experimental techniques and a great deal of empirical information. The Arabs were the most active workers in this great field of the black or magic arts. The elements were now called salt, sulphur and mercury, and mystic symbols were devised to guard the secret processes and the great key to all transmutation—the *philosopher's stone* which would convert base metals into gold.



Courtesy W. S. A. Singh

Fig. 3. Aristotle's idea of the origin of the four elements. The basic substance "hyle" had four properties and the action of any pair would produce one of the four elements shown.

Courtesy Fisher Scientific Co.

Fig. 4. Paracelsus (1493-1541) founded the school of medical chemistry. He believed in the philosopher's stone and sought the elixir of life.

4. Medical chemistry. Weary of the futile search for the philosopher's stone others turned to the search for the *elixir of life* which would give man eternal youth. This turned men to the study of the effect of chemicals on the human body and finally to the use of reason in their application. Paracelsus successfully used many chemicals to effect the cure of disease and medical men became chemical investigators. Van Helmont was one of the great investigators at the close of the period and he was probably the first to recognize a *gas* as a form of matter. He distinguished between air, carbon dioxide, hydrogen and marsh gas.

5. Modern chemistry. With the spread of the Renaissance, men of learning began to pursue the study of chemistry. Robert Boyle placed the term *element* on a sound experimental basis by stating that it was a substance which could not be divided into simpler substances by chemical means. To establish truth he propounded a logical method of verifying all

Courtesy Ayerst, McKenna & Harrison

Fig. 5. A modern research and control laboratory.

predictions. This method is the basic procedure for establishing scientific truth. There are five steps, which may not all be required in any one case, but the idea of verifying every prediction by a crucial experiment must be present or the method cannot be called the *scientific method.*

Step I. Systematic observation of facts. Each factor affecting a quantity is studied separately while all the others are held constant.

Step II. Recording the data. The important thing is that the observed *facts* must be accepted whether or not they suit any preconceived idea. The facts are classified in such a manner as to show dissimilarities and similarities as well as trends of behaviour.

Step III. Making a generalization. The trend of the data may make a generalization possible. It is a statement of a regularity found in the behaviour of nature.

Step IV. Forming a hypothesis. The above three steps employed the inductive method. Now the method of deduction may be employed and certain reasonable assumptions made about the nature of matter. For example, a gas may be assumed to consist of extremely small particles in

wild chaotic motion. From known laws of physics and by using mathematical procedures certain generalizations about gases may be predicted.

Step V. Verification of predictions. An experiment is then devised to see if the predicted result occurs. Confidence is increased and the theory may be accepted as a law or fact about nature if no exceptions are ever found.

6. Combustion. The story of how this scientific method was used to establish the chemical nature of fire is the best short illustration of how it was applied, but this whole book is an illustration of its use.

Step I to Step III. Facts and generalizations about combustion. Multitudes of isolated observations about combustion and calcination were available but few controlled experiments had been recorded. It was clear that some substances virtually disappeared on burning (*combustion*) and metals formed an ash (*calcination*). The ash was found to be heavier than the original metal. Air was found to be necessary unless a substance which could produce an air was present but not all of the air was used up in burning.

Step IV. Two hypotheses. Robert Hooke, John Mayow and Jean Rey thought that burning was due to the union of the substances with a part of the air but they could not tie their ideas down to a clear explanation. Becher and Stahl proposed that combustion and calcination were due to a combustible principle called *phlogiston* which escaped on burning. One of these two rival hypotheses had to be disproved by crucial experiments. This was Step V, and this step is outlined in the next three sections.

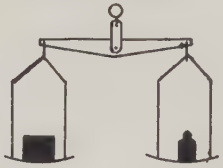
7. The phlogiston theory. This theory assumed that phlogiston was present in all combustible bodies, and that it was lost when the substance burned. It correlated a great many phenomena and gave them an apparently satisfactory explanation if certain objections were ignored. These were:

(1) Phlogiston was never isolated and collected. (2) The loss of a substance could not account for an increase in weight.

THE RIDDLE OF FIRE

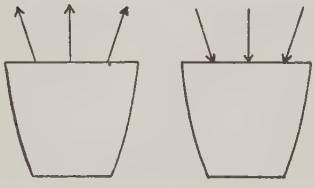
1. EARLY FACTS
   1. MANY NON-METALS LEAVE NO ASH WHEN BURNED
   2. METALS LEAVE A CALX HEAVIER THAN THE METAL

2. RECORDED DATA
   1. BEFORE BURNING

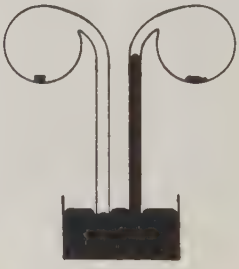


   2. AFTER BURNING

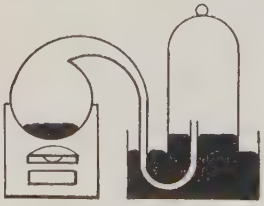
3. HYPOTHESES
   1. PHLOGISTON MOVEMENT

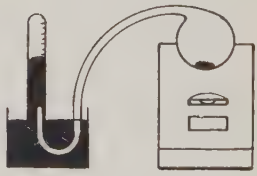


   2. UNION WITH OXYGEN



4. VERIFICATION OF OXYGEN THEORY
   1. MERCURY ABSORBED 8 ML. FROM AIR TO FORM 45 GRAINS OF RED CALX.
   2. THE 45 GRAINS OF RED CALX YIELDED 8 ML. OF OXYGEN.





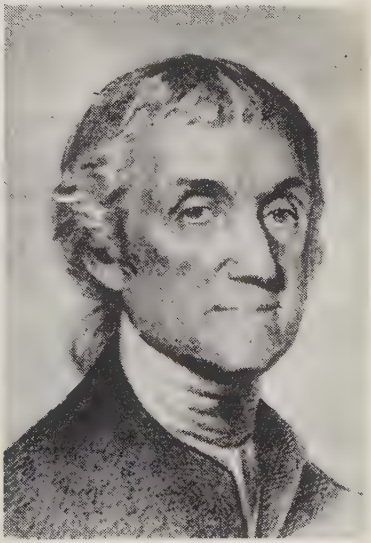
5. CONCLUSIONS
   1. PART OF THE AIR CAN SUPPORT COMBUSTION.
   2. SUBSTANCES COMBINE WITH OXYGEN WHEN THEY BURN IN AIR,
   3. THE PHLOGISTON IDEA IS NOT CORRECT.

FIG. 6.

The lack of ability to isolate the substance could easily be explained by the want of techniques for capturing flames but the increase in weight of metals by the loss of phlogiston was very awkward. The only explanation was that phlogiston must have a "negative weight" so as to buoy up the pure metal. This explanation was quite impossible. The usual method of rationalization was to ignore the objection or to say it was a matter of physics and not of chemistry. The phlogistic explanations became more complicated as new gases were identified.

Courtesy Brown Brothers

Fig. 7.



Courtesy Fisher Scientific Co.

Fig. 8.

Fig. 7. Carl Wilhelm Scheele (1742-1786), a poor apothecary in Sweden, who was among the first to recognize the nature of air and to prepare oxygen, nitric oxide, chlorine, hydrogen fluoride and many other gases and vapours.

Fig. 8. Joseph Priestley (1733-1804), British Unitarian minister and scientist, who collected gases over mercury and first reported the preparation of oxygen which he called "dephlogisticated air".

8. The discovery of oxygen. It was in the search for an answer to this problem of combustion that Carl Wilhelm

Scheele made the discovery of oxygen in 1772 without realizing that it would solve the riddle of combustion.

A few years later, on the 1st of August, 1775, a British Unitarian minister and amateur scientist, Joseph Priestley, prepared oxygen (dephlogisticated air) from mercuric oxide by means of a twelve-inch burning lens lent to him by his friend Warltire. He collected gases over mercury and firmly established the fact that several different airs (gases) exist, each with definite properties.

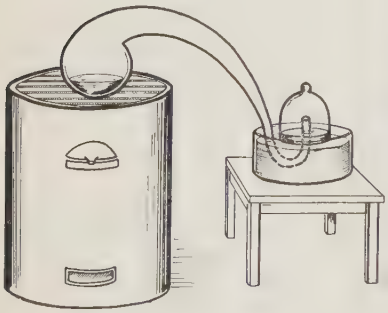
Each of these men failed to use oxygen to demonstrate the nature of combustion because they did not see the connection between the gain in weight and the absorption of oxygen.

9. Lavoisier establishes the oxygen theory. About the time Scheele discovered oxygen (1772), Lavoisier reviewed all the earlier experiments in a more precise manner. He verified Rey's conclusion (1630) that metals increase in weight because a part of the air is absorbed. By showing that calcination proceeds only until *a certain amount of the air is absorbed* he showed that combustion or calcination takes something from the air.

Lavoisier is called the "father of quantitative chemistry" because he proved his conclusions by accurate weighing. He performed experiments on tin by weighing it in *sealed* retorts. He found no change in weight when tin changed to tin oxide in a closed vessel. In October of 1774, Priestley visited Paris and told Lavoisier of his discovery of oxygen. Lavoisier saw the importance of this discovery to his anti-phlogistic theory. He set out to prove that dephlogisticated air (oxygen) is absorbed in the calcination of metals. His famous experiment which proved the nature of combustion and calcination is described in his *Traite de Chemie* (1789).

He placed a little pure mercury in a small glass retort connected to a bell-jar (see Fig. 9). The volume of air enclosed

in the bell-jar and the retort was 50 ml. The mercury was heated well below its boiling point and soon red flecks and then red scales of calx appeared on the surface. The heating was continued for twelve days or until no more red calx would form, and the volume of the air was measured. The air now occupied 42 ml., a decrease of 8 ml., and would no longer support combustion or respiration. Lavoisier called this part of the air "azote" meaning lazy. The red calx was collected and transferred to a tiny retort connected to another bell-jar filled with mercury. The calx was heated to over 300°C. where it slowly changed to pure mercury once more, evolving 8 ml. of Priestley's "dephlogisticated air". *The fact that calcination is a chemical combination with oxygen had been proven.*



Courtesy W. S. A. Singh

Fig. 9.

Courtesy Fisher Scientific Co.

Fig. 10.

Fig. 9. Lavoisier's apparatus for studying the removal of oxygen from air by hot mercury.

Fig. 10. Antoine Laurent Lavoisier (1743-1794), brilliant French chemist, who established the oxygen theory of combustion and modern quantitative methods.

Lavoisier set about showing how such substances as sulphur, phosphorous and carbon likewise use oxygen from the air for their combustion. When he had collected all the

data he could make the generalizations which constitute the oxygen theory of combustion.

1. Substances burn only in air or oxygen.
2. Combustion is a chemical combination with oxygen.

You can see how an untenable theory is disproved and an acceptable theory developed. Lavoisier collected accurate quantitative data, devised critical experiments to test his hypotheses and showed how his explanation was capable of accounting for all the known facts. This is the way of the scientific method. A theory must also be able to account for each new fact as it is discovered.

Question Summary

1. Describe briefly man's struggle for knowledge of matter.
2. What were some of the practical arts of the early chemists?
3. Define alchemy. What contributions did it make to chemical knowledge?
4. How was medical chemistry an improvement on alchemy?
5. Describe the basic method of operation of modern chemistry.
6. What were the early known facts about combustion?
7. How did the phlogiston theory explain combustion?
8. How was oxygen discovered?
9. Describe how Lavoisier established the oxygen theory of combustion.

Chapter 2

The General Behaviour of Matter

1. Introduction. You have made a flying trip over the centuries when man was struggling to secure a foothold of understanding on the mountain side of matter's nature. You have observed his fantastic but unsubstantiated "dreams" about the nature of matter, and how he finally devised a method for digging out the secrets of nature. We now enter the base camp of the chemical expedition which will take you on to further discoveries.

2. Matter and its three states. Matter cannot be defined because our senses recognize it as a reality. We say this because it occupies space and has mass or weight. To use a common expression, it is the stuff of which the world is made and we recognize it by means of our senses as existing in three *states.*

Man distinguished early the *liquid state* from the *solid state. When matter has a definite volume and a definite shape*, we say that it is in the *solid state. When it has a definite volume but takes the shape of the containing vessel*, we say that it is in the *liquid state.*

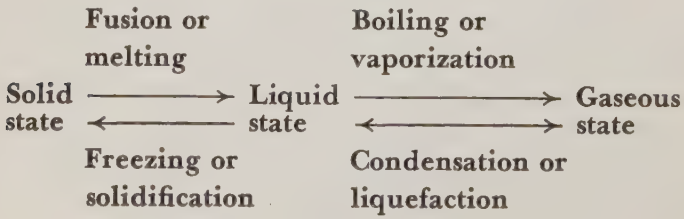
Most substances can be changed from the solid to the liquid state simply by heating them and the temperature at which this change occurs is called the *melting point.* Some substances have a sharp melting point and are known as *crystalline substances.* Other substances soften and lose their definite shape over a range of temperature. These are often only *supercooled liquids.* Glass, asphalt and wax are examples of such substances. The reverse change from liquid to solid is known as *freezing* or *solidification.* The *freezing point* is thus

the same temperature as the melting point. We can summarize these changes in state by an equation.

$$\text{Solid state} + \text{Energy} \underset{\text{Solidification}}{\overset{\text{Melting}}{\rightleftharpoons}} \text{Liquid state}$$

It was hard for man to realize the gaseous state of matter as it was usually invisible, and we trust our sight more than any of our other senses. You know that the gaseous state is real because you ride on the air-filled tires of your car or bicycle. You feel it in a strong wind and you know that something must carry the raindrops, sleet or snow. *Gases have neither a definite volume nor a definite shape, and will fill completely any vessel in which they may be placed.*

Liquids and gases are known as *fluids*, from the Latin word *fluere*, because they will flow into every corner of a container. Liquids can be converted to gases by the addition of energy in the form of heat and this process is known as *vaporization*. Gases can be converted into liquids by the removal of the heat, and this reverse process is known as *condensation* or *liquefaction*. If we can see the bubbles of vapour forming in a liquid and rising to the surface we say it is *boiling* and the temperature at which this visible change occurs is known as the *boiling point*. We can represent the transition between the three states by means of a diagram.



When some substances are heated they can pass from the solid to the gaseous state without becoming liquid. Such substances are said to *sublime* and the process is called *sublimation*. Iodine crystals sublime when they are heated and the process of sublimation gives clouds of a beautiful dense violet vapour which is very irritating to the nostrils.

3. Recognition of substances. If we examine the many substances which surround us we notice that we are able to recognize them when we see them by means of definite characteristics. We examine their colour, shape, size, density, strength, taste, odour. We also note the manner in which they react to their surroundings and their influence upon other substances. These characteristics by which we identify and recognize substances are known as their *properties*. By examining and recording the properties of various substances we are able to classify them. We find that some of them, such as lead, iron and mercury appear to be the same throughout, and we say that they are *homogeneous*. Others, such as concrete, granite and sand are made up of different parts and are *heterogeneous*. In our examination of matter we have learned to *break it down into other substances* so that we may learn how it is built up, and this process is known as *analysis*. We have also learned how to *construct new substances by building them from their parts*. This process of construction is known as *synthesis*. In this examination of substances we have learned that matter can be changed into other forms although it can never be destroyed. We may classify the changes which a substance can undergo into physical changes, and chemical changes. Such a classification is shown in Table 1 (see page 16).

4. Physical change. If we place one end of a rod of iron in a hot fire we notice that there are many changes. The end becomes red and finally almost white, the end which we are holding in our hand becomes hot, and if we measured

TABLE 1—ILLUSTRATIONS OF PHYSICAL AND CHEMICAL CHANGES

Substance	*Physical change*	*Chemical change*
Wooden house	Blown down in storm	Burned in fire
Copper wire	Cut into pieces	Heated in oxygen
Paper	Torn into pieces	Burned
Food	Chewed by teeth	Digested in stomach
Iron	Broken into pieces	Rusted
Leaves	Fallen from tree	Decayed on ground
Tobacco	Rolled into cigarette	Smoked
Iron and sulphur	Mixed together	Heated together
Cloth	Torn into pieces	Burned
Water	Frozen to ice	Decomposed by electricity
Cake ingredients	Mixed together	Cooked

the length of the rod we would find that it had become longer. There have been definite changes in the matter of which the rod is made. If we remove the rod from the fire we find that it regains its original colour and appearance, it no longer feels hot to the touch, and we can show that it has recovered its original length. We still have the rod of iron. We have not produced a new substance. *A change of matter in which a new substance is not produced* is known as a *physical change*. The breaking of a pane of glass, the melting of ice, the boiling of water, are all physical changes.

5. Chemical changes. We are familiar with the burning of a match. Light and heat are given off and a charred stick is left. This stick is certainly not the same as the match because it is a new substance. A piece of iron left out of doors will turn to a pile of rust which is certainly a different substance from the original piece of iron. A current of electricity will decompose water into the two new substances, hydrogen and oxygen. In all of these changes a new substance has been produced. *A change of matter in which a new substance is produced* is known as a *chemical change*. The properties of substances that are concerned with physical changes are known as *physical properties*, while those connected with chemical changes are known as *chemical properties*.

6. Elements. If we carry out the analysis of substances by means of chemical changes, we can often discover other substances which are more simple in their composition than the original material. In the course of our examination we find that there are some substances like iron, sulphur, tin, lead, silver and gold, which *cannot be broken down into more simple substances by chemical means*. Such substances are known as *elements* and ninety-six of them have been discovered to date. The elements are the building bricks of the universe and *chemistry* is the science which deals with the elements and the substances which are produced by their union with one another.

The elements may be divided into *metals* and *non-metals*. The metals are characterized by their lustre, their high density and their ability to conduct heat and electricity. The non-metals do not have these physical properties to a marked extent. They may be gases, as hydrogen, oxygen and nitrogen; or solids, like sulphur, carbon and silicon. There are two elements which are liquid at room temperature, the metal mercury and the non-metal bromine.

The abundance of the elements in the crust of the earth is illustrated diagramatically in Fig. 11 (see page 18).

7. Compounds. In the examination of substances we find some which can be broken down into more simple substances, but *always have their own characteristic properties and a constant composition by weight*. These substances are known as *compounds*. It is a characteristic property of all pure compounds that their component parts are always present in the same ratio.

8. Mixtures. We are familiar with many substances, such as concrete, granite and sand, which are heterogeneous. If we examine them we find that they can be broken down into more simple substances, but their component parts are not present in any definite proportion by weight. We also find

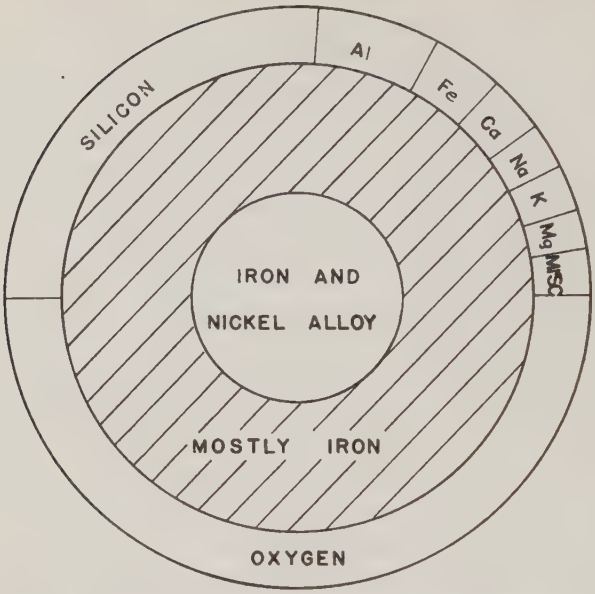


Fig. 11. The relative abundance of the elements in the earth's crust is shown in the outer ring by the size of the pieces. The core of the earth is believed to be mostly iron and nickel.

that their *properties are not characteristic but will vary with the nature and composition of the components.* These substances are known as *mixtures.* It is a characteristic property of all mixtures that their component parts may be present in *any* proportions by weight. The substances which compose the mixtures are said to be *mixed* together. Distinguish carefully between the words "mixed" and "combined".

9. The difference between compounds and mixtures. Let us consider the two familiar elements, iron and sulphur. Iron is grey-black in colour, is insoluble in the organic liquid, carbon disulphide, and is attracted to a magnet. Sulphur is bright yellow in colour, is soluble in carbon disulphide, and it is not attracted by a magnet. If we place a quantity of these elements in the form of a fine powder upon a sheet of

paper and stir them together we produce a *mixture*. We find that the colour is somewhere between the yellow of sulphur and the grey-black of iron, and is dependent upon the quantity of each element that is present.

If we pass a magnet over the mass we find that the particles of iron are attracted to the magnet and may be thus removed from the pile of powder. If we place the mixture in the liquid carbon disulphide, we find that the sulphur dissolves while the iron does not. If we analyse the mixture we find that the iron and sulphur are not present in definite proportions, since if we prepare another mixture of iron and sulphur, we find that the proportions of the iron and sulphur may be different. It is apparent that the mixture consists of particles of iron and sulphur lying side by side, each contributing their own properties to the properties of the mixture.

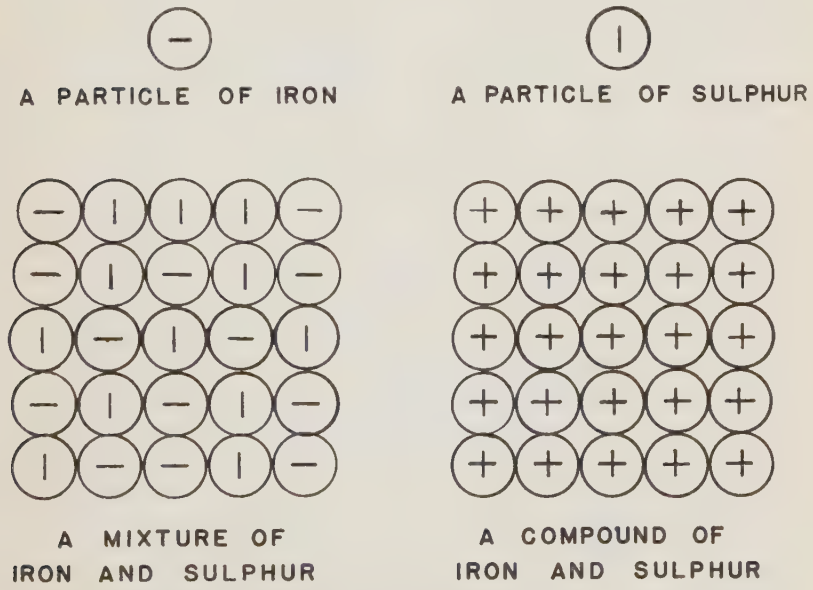
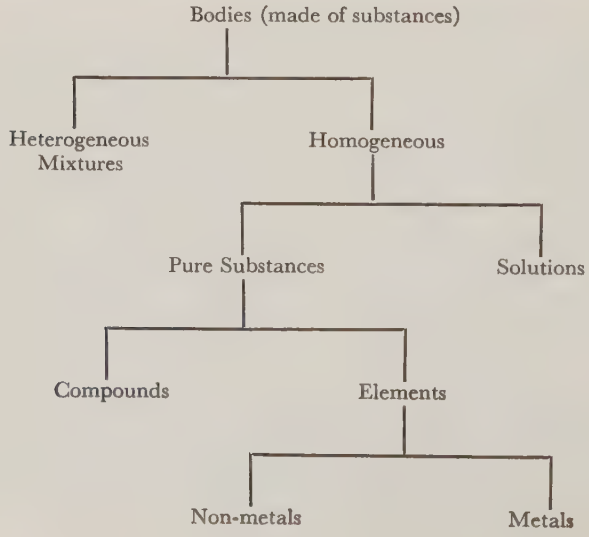


Fig. 12. The difference between a mixture and a compound. A compound is homogeneous and has only particles of a new substance.

If we place the mixture of iron and sulphur in a test tube and heat it we see that it commences to glow by itself. When all reaction ceases we allow it to cool and examine it. We break the tube and find that we have a grey-black mass which appears to be homogeneous. We can no longer distinguish the separate particles of iron and sulphur by means of our eyes. If we powder the mass and pass a magnet over it we find that it is not attracted to the magnet and we cannot remove any particles of iron. If we place the mass in carbon disulphide we find that it does not dissolve. If we analyse the substance we find that it contains 63.5 per cent of iron and 36.5 per cent of sulphur. We have made a new substance in which the iron and sulphur are united with one another. The idea of a compound and a mixture is shown in Fig. 12.

10. Solutions. When sugar is dissolved in water it seems to disappear. The solution is homogeneous, but it does not have the definite composition which is characteristic of a new substance. A solution is a homogeneous mixture of two



or more substances where the dispersed particles are so minute that they escape ordinary physical detection.

The labours of many centuries enable us to systematize and classify material bodies, as shown on page 20.

Pure substances whether compounds or elements always have a constant composition.

Question Summary

1. How did man use his method of inquiry to determine the nature of fire?

2. (*a*) Name the three states of matter and explain how you would distinguish between them.
(*b*) What are fluids and how do they get their name?

3. (*a*) What is meant by the properties of a substance?
(*b*) Define analysis and synthesis.

4. (*a*) Define a physical change.
(*b*) Give five examples of physical changes.

5. (*a*) Define a chemical change.
(*b*) Give five examples of chemical change.

6. (*a*) Define an element.
(*b*) What is the difference between metals and non-metals?
(*c*) Name some of the more abundant elements found in the earth's crust.
(*d*) Why are some of the other elements not found free?

7. Define a compound.

8. Define a mixture.

9. (*a*) State the difference between a compound and a mixture.
(*b*) How might you determine whether a given substance was a compound or a mixture?

10. From what you have learned in this chapter, give definitions of the following terms: matter, solid, liquid, gas, melting point, vaporization, fluid, physical properties, chemical properties, condensation, solidifaction, crystalline solid, homogeneous, heterogeneous, sublimation, solution, pure substance, element, compound, mixture.

Chapter 3

Water as a Reference Chemical

1. Importance. Water is the most important chemical in the world because it acts as the carrier of life itself. In the liquid state we find it both on the surface of the earth and in the cells of all living things. Table 2 shows that many of our foods are mainly composed of water.

TABLE 2—WATER CONTENT OF SOME FOODS

Food	*Percentage of Water*	*Food*	*Percentage of Water*
Beef (no fat)	73.8	Wheat Flour	11.9
Ham	53.5	Bread, white	35.3
Salmon	64.6	Beans, dried	12.6
Eggs	73.7	Corn, green	75.4
Milk	87.0	Potatoes	78.3
Butter	11.0	Tomatoes	94.3
Oatmeal	7.3	Apples	84.6
Rice	12.6		

In the gaseous or vapour state water forms about two per cent of the earth's atmosphere. This water vapour condenses to give us the rain, snow, hail and clouds. In the solid state it exists in the form of glaciers, polar ice caps and icebergs. The balance of water between the atmosphere and the earth is known as the water cycle. See Fig. 13.

Water in the solid, liquid or gaseous states is called "free" or "uncombined water", since it is not in the chemical constitution of other substances. Water also exists in the combined state in many compounds. These are known as *hydrates* and the water in them is called *water of hydration.* A great many salts combine with water as they crystallize from solution and they often lose their familiar crystal form

when the water is removed. Calcium chloride and copper sulphate are familiar examples of hydrated salts.

Water is so fundamental and familiar that man has made its physical properties a reference standard for the measurement of such characteristics of matter as density, heat capacity, temperature and even pressure.

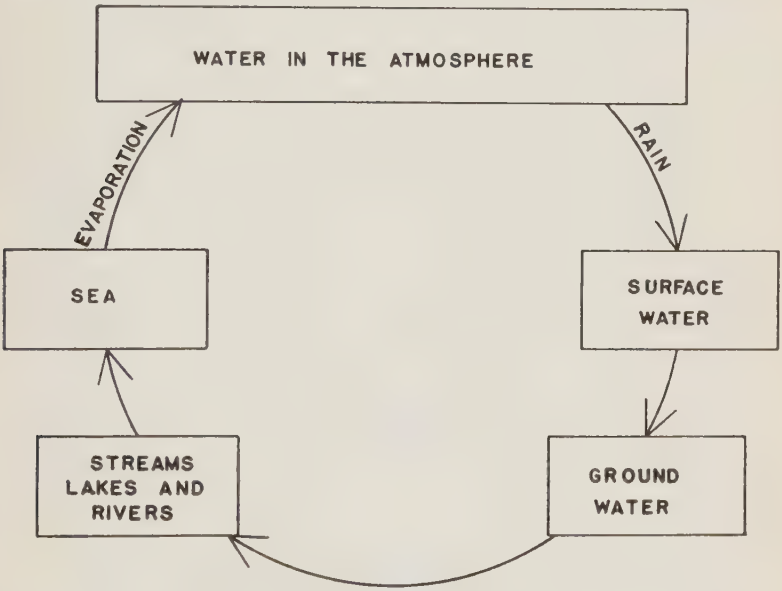


Fig. 13. The water cycle in nature.

2. Physical properties. Pure water is usually described as colourless, odourless and tasteless. Its transparency and lack of colour have made it a starting-point for the measurement of colour. Actually large masses of it show a greenish-blue colour. Any odour it contains is due to its remarkable tendency to dissolve all things to some extent, so that absolutely pure water is as hard to get as a perfect vacuum. If you have ever tasted pure distilled water you know how repulsive it is because of what we call its "flat" taste. This is because pure water is tasteless. What we call "good" drinking water contains dissolved salts, oxygen and other impurities.

3. Temperature measurement. The freezing point and boiling point of water are so characteristic that they determine the fixed points on our temperature scales. They are points of reference for the relative hotness or coldness of other forms of matter. The temperature at which water changes to ice is 0° on the Centigrade scale. The temperature at which pure water changes into vapour under an external pressure of 760 mm. of mercury is marked as 100° on the same scale. Fahrenheit erroneously believed that the lowest temperature he could reach by mixing ice and salt was a basic zero point. We now use the freezing point of pure water to mark the 32° point on his scale and the boiling point of water to mark the 212° point. The Fahrenheit scale has 180 divisions between the freezing and boiling points of water but the Centigrade scale has only 100 divisions. There are thus nine divisions on the Fahrenheit scale for every five on the Centigrade scale.

One of the most useful skills is to be able to convert from one scale to the other. The following method is based on the fact that −40°C. is −40°F.

1. To change Centigrade temperatures to Fahrenheit.
   (*i*) Add 40 to the Centigrade reading.
   (*ii*) Multiply the sum by $\frac{9}{5}$.
   (*iii*) Subtract 40 to find the Fahrenheit reading.

Example: Convert 20°C. to Fahrenheit.
   (*i*) 20 plus 40 equals 60
   (*ii*) 60 × $\frac{9}{5}$ equals 108
   (*iii*) 108 minus 40 equals 68°F.

2. To change Fahrenheit temperatures to Centigrade.
   (*i*) Add 40 to the Fahrenheit reading.
   (*ii*) Multiply the sum by $\frac{5}{9}$.
   (*iii*) Subtract 40 to find the Centigrade reading.

Example: Convert 950°F. to Centigrade.
   (*i*) 950 plus 40 equals 990
   (*ii*) 990 × $\frac{5}{9}$ equals 550
   (*iii*) 550 minus 40 equals 510°C.

You will note that it is necessary to add 40, multiply by the appropriate factor and subtract 40 to make the conversion.

4. Density and specific gravity. In the measurement of metric quantities there are three fundamental units, the centimetre of length (cm.), the gram of weight (g.) and the second of time (sec.). Table 3 shows the multiples and fractions of the centimetre and the gram.

TABLE 3—METRIC UNITS OF LENGTH AND WEIGHT

1 kilometre	1000 m.	1 kilogram	=	1000 g.
1 hectometre	100 m.	1 hectogram	=	100 g.
1 dekametre	10 m.	1 dekagram	=	10 g.
1 metre	100 cm.	1 gram	=	1 g.
1 decimetre	10 cm.	1 decigram	=	1/10 g.
1 centimetre	1 cm.	1 centigram	=	1/100 g.
1 millimetre	1/10 cm.	1 milligram	=	1/1000 g.

NOTE: one inch = 2.54 cm. and one pound = 454 g.

The unit of volume for solids is the cubic centimetre ($cm.^3$) but the unit of volume for gases and liquids is the litre, which is almost exactly 1000 $cm.^3$. The fractions of a litre have the same prefixes as the fractions of a metre. You should note carefully the meaning of such prefixes as kilo-, deci-, centi- and milli-. All other units are powers and combinations of the fundamental units.

Water is used as a standard to relate two of these units to one another. *The density of any substance is the weight of a unit volume of that substance. One cubic centimetre ($cm.^3$) of water at 4°C.* is almost exactly one millilitre (1/1000 litre) and it *weighs one gram.* The density of water at 4°C. is thus a unit in which the density of other substances may be expressed. When we do this we say we are giving the *specific gravity* of the substance.

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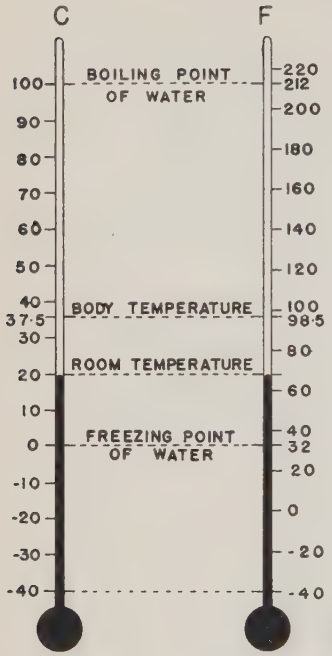


Fig. 14. Centigrade and Fahrenheit temperature scales.

Fig. 15. The relative volumes of equal weights of different metals.

TABLE 4—SPECIFIC GRAVITY OF SOME COMMON ELEMENTS

Element	*Sp. Gr.*	*Element*	*Sp. Gr.*
Aluminum	2.7	Magnesium	1.74
Calcium	1.54	Mercury	13.56
Copper	8.9	Iron	7.21
Gold	19.3	Sodium	0.97
Lead	11.34	Zinc	7.1

Example: The density of mercury is 13.56 g/cm.^{3}. It is thus 13.56 times as dense as water so we say its specific gravity is 13.56. *The specific gravity of a substance is its density compared to the density of water.* The units of measurement cancel one another in the comparison so specific gravity is only a number.

Fig. 15 shows the relative volumes of the same weight of different metals.

The *pressure of the atmosphere* is measured by the height of a liquid it will support in an evacuated space. It is well known that water can only be "sucked" up about thirty feet by a suction pump. Such a long column of water is inconvenient so we use the height of a column of mercury to measure atmospheric pressures, because the mercury column will only be 1/13.56 times as long. The normal atmosphere at sea level will lift into a vacuum a column of mercury 760 mm. long.

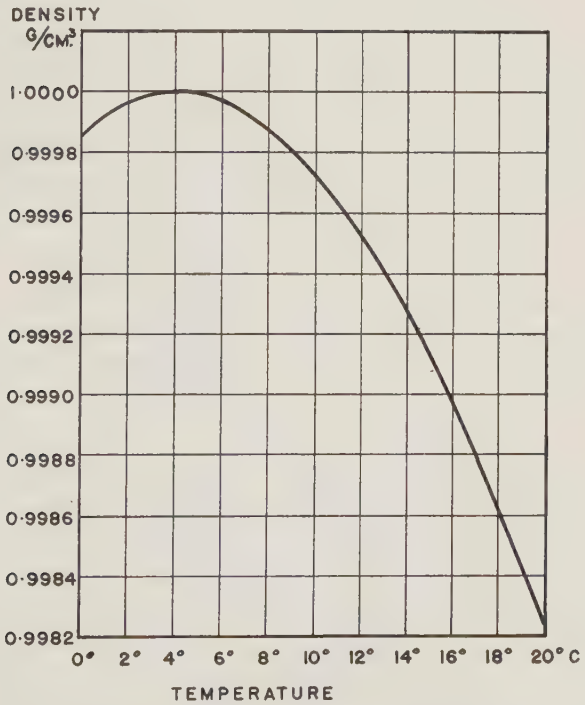


Fig. 16. The change in the density of water with temperature. Water either colder or warmer than water at 4°C. will float on it. This makes deep waters cool and enables ice to form at the surface.

Water has its greatest density at 4°C. and it becomes less dense as it is cooled below 4°C. or heated above 4°C. Fig. 16 shows the amount of the change. Since the denser water sinks to the bottom, water cooler than 4°C. rises to the surface of lakes and rivers. There is a decrease in density of about ten per cent when water changes into the solid form so it freezes and remains on the surface. If it were not for this abnormal behaviour our lakes and rivers would freeze solid from the bottom up and all aquatic life would cease to exist.

5. Measurement of heat. *Water is so universal that the heat required to raise the temperature of one gram of water one degree centigrade is the unit of heat, the calorie.* The specific heat of water is 1 and of copper 0.095. Thus for the same weights of water and copper, the water requires over ten times as much heat to raise its temperature by the same amount.

TABLE 5—SPECIFIC HEATS OF SOME COMMON SUBSTANCES

Substance	*Sp. Heat* (cal./g.)	*Substance*	*Sp. Heat* (cal./g.)
Water	1.000	Gold	0.0324
Iron	0.112	Sulphur	0.203
Copper	0.095	Silver	0.057
Diamond	0.141	Sodium	0.293
Wax	0.5	Magnesium	0.245

When water changes from a liquid at 100°C. to a vapour at 100°C. it absorbs about 540 calories of heat per gram with no change of temperature. This heat is called the *heat of vaporization.*

6. Water as a solvent. Water is the nearest approach to a universal solvent. Its ability to dissolve all substances to some extent causes us to characterize substances by their solubility. The solubility is the *amount* which can be dissolved in a given volume of solvent at a certain temperature. Unless we specify some other solvent we mean the solubility in water.

Just what happens when a substance dissolves in water or any solvent is a story we cannot tell here but the substance which disappears, the *solute*, is said to be *in solution*. We can sometimes evaporate the solvent and leave the dissolved substance as a residue. Thus:

Solute + Solvent = Solution

If the dissolved substance is removed by a process of evaporation in an arrangement whereby the vapour may be condensed to a liquid in another vessel the process is called *distillation*. This is the meaning of the term *distilled water*. It should be free from its impurities.

When one substance is finely dispersed in another substance but it is still possible to detect the particles by means of a beam of light, we say that it is not a true solution but merely a *suspension* or *colloid*. Many of our puddings, jellies, beverages and dressings are colloids. True solutions are devoid of particles large enough to be detectable. They are therefore homogeneous and distinguishable from colloids by means of a beam of light (see Chap. 26).

If the suspended particles are too large to pass through the pores of a paper, cloth, screen, or pad of fine fibres, they may be removed from their dispersing medium by the process called *filtration* (see Fig. 17). Dissolved material or colloidal material can not be removed in this way.

7. Purification of water. Ordinary tap water is far from being chemically pure water but we expect it to be safe water. Pure water is tasteless so we wish drinking water to have traces of salts and dissolved gases but no harmful bacteria, bitter-tasting salts or unpleasant odours. Sea-water contains too much salt. Rain-water contains too few salts and sometimes contains traces of dissolved materials from the roofs and gutters. Water from wells into which surface water cannot drain directly usually contains enough salts

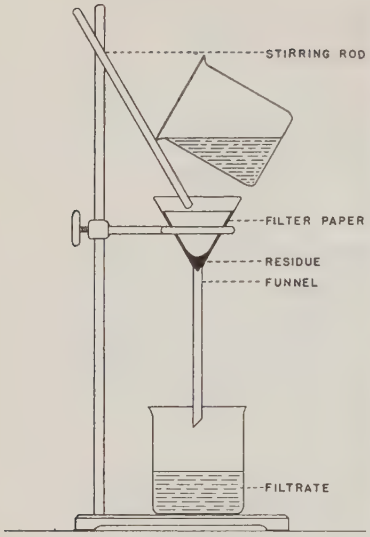
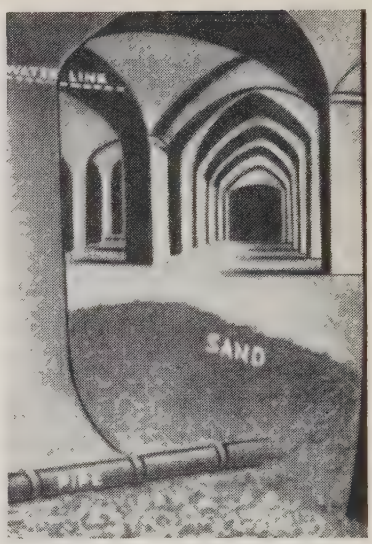


Fig. 17. Laboratory filtration. The stirring rod is used to guide the solution into the filter paper. The suspended solids caught on the paper form the residue and the solution which passes through is the filtrate.



From Black & Conant: "New Practical Chemistry", courtesy The Macmillan Company

Fig. 18. Filtering drinking water through beds of sand under a concrete roof. The filtered water is pumped from the porous drain pipes to the reservoir. Chemicals are added to help trap impurities.

to give it a pleasant flavour. Surface water is used to supply most of the large cities. It contains dissolved salts from the surrounding watershed but it may be contaminated by germs, coloured matter, living organisms and suspended impurities. Such water often has to be treated before it is suitable for drinking water.

If the harmful bacteria in the water are destroyed by chlorine or some other disinfectant the water is usually safe to drink but it may not be pleasant. To remove undesirable matter the water is usually filtered through sand filters (see Fig. 18). Before it is filtered it is often treated with adsorbent charcoal to remove odours and with alum to collect together the extremely fine particles which would pass through

the filters. You will learn more about this process when you study the chemistry of aluminum.

If the dissolved salts must be removed then distillation or ion-exchange may be used. These are usually too expensive except for special purposes such as laboratory work or storage batteries.

Question Summary

1. (*a*) Why is water the most important chemical?
(*b*) Who disproved the theory that water is an "element"? How did he do it?

2. Why is it so difficult to make absolutely pure water? What makes it palatable?

3. Explain how the freezing point and boiling point of water are used to fix the scale on a thermometer.

4. (*a*) Give the meaning of the prefixes: kilo-, deci-, centi- and milli-.
(*b*) How is the density of water used to relate its weight to its volume in a simple manner?
(*c*) What is the difference between density and specific gravity?
(*d*) Does freezing purify natural waters?

5. What is meant by the term specific heat?

6. (*a*) What kind of a vessel would be required for a universal solvent? Can this question be answered? Explain.
(*b*) Precisely define an aqueous solution.
(*c*) Why is rain-water the purest form of natural water?

7. What methods are available for water purification?

Problems

1. (*a*) Convert the following Centigrade temperatures to Fahrenheit: −40°, −5°, 10°, 50°, 100°, 500°, 1000°, 1550°, 2000°, 3000°.
(*b*) Convert the following Fahrenheit temperatures to Centigrade: −40°, 32°, 68°, 212°, 392°, 752°, 1391°, 2000°, 5000°, 10,000°.

2. *One kilogram* is about *2.2 pounds.*
(*a*) How many grams weigh one pound?
(*b*) Calculate your weight in kilograms.
(*c*) What is the weight of one litre of water in avoirdupois ounces?
(*d*) How many centimetres are equal to 4 inches?; to 1 foot?; to 1 yard?

(*e*) How many milligrams are in the following quantities if 7000 grains = 1 pound?

(*i*) 1 grain; (*ii*) 15.43 grains; (*iii*) 0.02 grains.

(*f*) The inside diameter of a test tube is 0.5 inches and it is five inches long. How many millilitres will it hold?

3. (*a*) Find the volume of the following in millilitres:

(*i*) one kilogram of iron; (*ii*) one pound of copper; (*iii*) one ounce of sodium; (*iv*) one carat of gold (3.17 grains).

(*b*) Find the weights of the following volumes:

(*i*) one litre of water at 4°C.; (*ii*) one cubic decimetre of lead; (*iii*) three cubic feet of water; (*iv*) 15 cubic centimetres of lead.

4. How many calories of heat is required to heat

(*i*) one litre of water from 5°C. to 25°C.; (*ii*) four kilos of copper from −20°C. to 55°C.; (*iii*) five grams of sulphur from 7°C. to 97°C.?

Chapter **4**

The Atmosphere and Nitrogen

1. Introduction. The mixture of gases surrounding the earth is known as the *atmosphere* and commonly called the *air*. The word *air* is used generally to denote smaller quantities, so we speak of the air in a vessel rather than the atmosphere. Air was regarded by the ancients as an element, and when the various gases, such as oxygen, hydrogen and carbon dioxide were discovered they were thought to be special kinds of air. Thus oxygen was known as "dephlogisticated air"; hydrogen as "inflammable air"; and carbon dioxide as "fixed air". When you realize that a study of gases requires special training and careful work, and that many gases are colourless, odourless and tasteless, it is not surprising that the early experimenters could not distinguish one gas from another.

2. The composition of the atmosphere. The composition of the atmosphere varies slightly with the location and with the height above sea level. The composition may be expressed either by volume or by weight. The following table gives the average composition of *dry* air at sea level.

In addition to the substances listed in the table, (over) the air contains varying amounts of water vapour. As one rises above sea level the amount of oxygen becomes less and the amount of nitrogen grows proportionately greater. Since oxygen is heavier than nitrogen, the change in the amount of oxygen could be due to the effect of gravity, and it is therefore believed that the amount of nitrogen grows less and the amount of hydrogen, which is the lightest gas, becomes

greater as one moves away from the earth. It might be possible that the outermost portions of the atmosphere consist of hydrogen alone.

TABLE 6—THE AVERAGE COMPOSITION OF DRY AIR

Name of gas	*Volume*	*Weight*
Nitrogen	78.03%	75.45%
Oxygen	21.00	23.20
Argon	0.93	1.30
Carbon dioxide	0.04	0.05
Hydrogen	Trace	Trace
Neon	Trace	Trace
Helium	Trace	Trace
Krypton	Trace	Trace
Xenon	Trace	Trace

The pressure of the air decreases from 760 mm. at sea level to about 40 mm. at a height of 10 miles, and the pressure continues to decrease as one goes farther away from the earth. At high altitudes there is not sufficient oxygen to sustain life, and high-flying aircraft must carry supplies of oxygen. Close to the surface of the earth, small amounts of various other substances may be found. Some of these substances are present because of local contamination, such as volcanic eruptions and industrial processes. Sodium chloride is present in the air over the ocean and near the sea coast and other substances are present because of the decay of organic material. Bacteria and yeast cells are present in the air and are responsible for the processes of fermentation and putrefaction.

3. The air is a mixture. With regard to the components oxygen and nitrogen the composition appears to be approximately constant, and there might be cause to believe that the atmosphere is a compound of at least these two gases. The following reasons, however, show that air must be a mixture.

(1) None of the known compounds of oxygen and nitrogen have a composition like that of air.

(2) There is not only considerable variation in composition with the location on the surface of the earth, but the change of composition with altitude shows that the atmosphere cannot be a compound.

(3) If air is passed through water proportionately more oxygen than nitrogen is dissolved. This would not be the case if the oxygen and nitrogen were combined.

(4) Changes in energy are associated with chemical change. If the components of the atmosphere are mixed at ordinary temperatures and pressures the mixture has all the properties of air, but there is no indication that energy is either absorbed or liberated.

(5) If liquid air is allowed to evaporate the different gases will boil off at different temperatures. No compound will act in this manner. If a gas which is a compound is liquefied, it will boil at a constant temperature until it evaporates completely.

4. Liquid air. Considerable work was done by Faraday and other experimenters on the liquefaction of gases. It was found that there were some gases, such as hydrogen, oxygen and nitrogen, which could not be liquefied; these gases were accordingly termed the "permanent gases". In 1869, Andrews found that while carbon dioxide could be liquefied by pressure at various temperatures up to 31.4°C., it could not be liquefied if it were at a higher temperature. He then found that for each gas there is a certain temperature, which he termed the *critical temperature, above which the gas cannot be liquefied by pressure.* In the case of some gases the critical temperature is above room temperature while in the case of the permanent gases it is much lower. In 1885, Wroblewski prepared liquid oxygen, liquid hydrogen and liquid air. At first liquid air was a laboratory curiosity, but by 1891 it was available in sufficient quantity for low temperature experiments.

Liquid air is prepared by a combination of low temperature and high pressure as shown in Fig. 19. This is not a picture of the apparatus but is intended only to illustrate the principle.

The air is first purified by filtering out any suspended solids, such as dust. Since carbon dioxide and water vapour freeze at temperatures so much higher than do any of the other components they must be removed or they would clog the pipes. The purified air is compressed greatly and the heat of compression is removed by passing the compressed air through coils immersed in running water. The highly compressed air is then passed through a spiral tube and allowed to escape through a very small

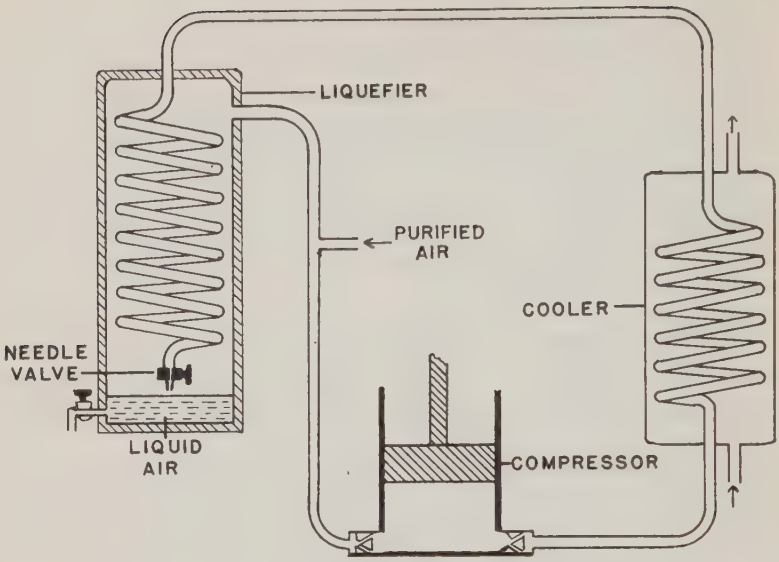


Fig. 19. The principle of liquid air machines.

opening known as the expansion valve. Whenever a highly compressed gas is allowed to expand its particles require energy to enable them to escape from the attraction of their neighbours. If this energy is not supplied from an outside source they will use up some of their own kinetic energy, which is the energy they possess by virtue of their motion. As the temperature of a gas is due to the average kinetic energy of the particles, this loss of energy will result in a cooling of the gas after it has expanded. The expanded and cooled gas is then allowed to flow around the spiral tube leading to the expansion valve, thus helping to cool the compressed air which is on its way to the valve, and is then returned to the compressor to be put through the cycle again. As this cycle is repeated the air becomes cooler and cooler until it is below the critical temperature and will finally liquefy at the expansion valve. Once this occurs the formation of liquid air becomes rapid and the liquid may be collected. You will understand this explanation better after you study the kinetic theory of gases. Liquid air is used to provide low temperatures during scientific research, and it has an extensive industrial use in the production of oxygen and nitrogen.

NITROGEN

5. Introduction. In 1772 Daniel Rutherford found that when certain substances, such as phosphorus and carbon,

were burned in air the gas that remained after the combustion was different from the original air. He showed that this gas contained a portion that was absorbed by bubbling it through an alkali, and that the final residue would not support life or combustion and was inactive as compared with ordinary air. Scheele showed later that this gas which had been obtained by Rutherford was always present in the atmosphere. Lavoisier recognized it to be an element and gave it the name *azote*, by which name it is still known in France. In 1823, this element was named *nitrogen* by Chaptal because it was found to be a constituent of nitre, or potassium nitrate.

6. Occurrence. Nitrogen constitutes about four-fifths of the atmosphere where it exists in the free state. The nitrogen in the atmosphere acts as a diluent for the oxygen and if it were not there life as we know it would cease to exist. Oxidation would be too rapid, metals would corrode so quickly that their use would be impractical, and burning would be impossible to control.

Nitrogen is found in the combined state in the form of salts. The best-known deposit is that of sodium nitrate in Chile. The salt is known as *Chilean saltpetre* and is mined and sold for use in the manufacture of dyes, fertilizers and explosives. Nitrates are also found in some other parts of the world. Until the development of modern industrial processes for obtaining the gas from the air these natural deposits were of great economic importance.

Nitrogen is found in combination with other elements in complex substances known as proteins which are found in all animals and plants. The use of nitrogen in the structure of these proteins is the reason for the element being required in animal diets and in fertilizers. The proteins are used to build new tissue as it is required for the growth and maintenance of both animals and plants.

7. The nitrogen cycle. Nitrogen passes from one form to another in the course of natural events and we could start with nitrogen in the air and trace its passage through animals and plants until it returns to the atmosphere. This course of events is known as the *nitrogen cycle* and may be illustrated by the chart shown in Fig. 20. The nitrogen in the air is converted into plant proteins by the action of nitrogen-fixing bacteria and the plants themselves. These bacteria are on the roots of certain plants, such as legumes, and are

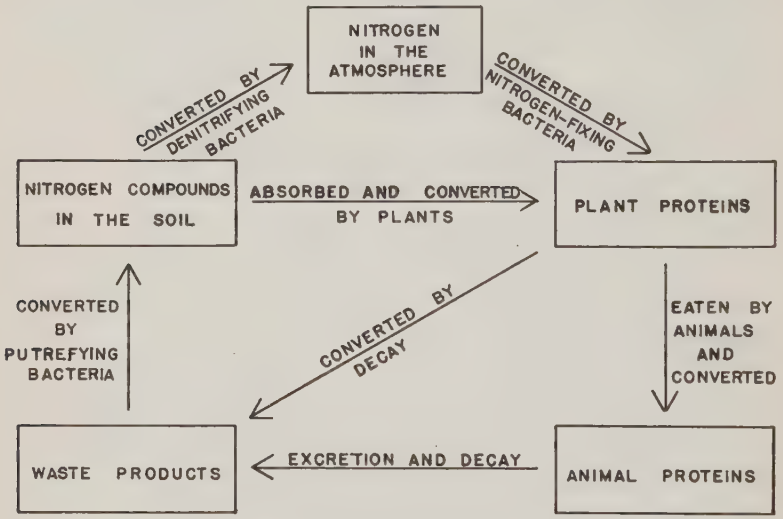


Fig. 20. The nitrogen cycle in nature.

found in the soil. Legumes have the property of fixing nitrogen in the soil and provide it as a fertilizer to crops. The continual growing and harvesting of crops will remove nitrogen as well as other elements from the soil, and the occasional growing of a crop of legumes will assist in returning nitrogen to the soil. The nitrogen compounds produced by the action of the bacteria are converted into proteins by the plants. The plants serve as food for animals and their nitrogen compounds are converted into animal protein. By

excretion and decay the animal proteins are in turn converted into waste products which may be returned to the soil or added as fertilizer. As can be seen on the chart some of these waste products come directly from the decay of plant proteins.

The waste products are acted upon by fertilizers and bacteria and produce nitrogen compounds in the soil. These compounds are absorbed by plants to form proteins and thus complete a cycle which need not include the nitrogen of the air at all. Other nitrogen compounds in the soil are decomposed by the denitrifying bacteria which are in the soil and the nitrogen produced by this decomposition escapes into the air to complete the larger cycle shown on the chart.

8. The preparation of nitrogen.

A. Laboratory Methods.

(1) *By the removal of oxygen from the air.* Nitrogen may be obtained from the air by removing the oxygen. If a piece of phosphorus is placed in air in a closed vessel over water and allowed to stand for some time, it will be noticed that the water will rise in the vessel, and the remaining gas will be found to be nitrogen together with whatever else was in the air except oxygen. This is shown in Fig. 21, where a piece of phosphorus is seen supported on the cork which is floating on the water which has risen inside the vessel.

If air is passed over heated copper the oxygen of the air will combine with the copper to form copper oxide and nitrogen will be left. These methods do not produce pure nitrogen as they remove only oxygen from the air, leaving the other constituents. However, as the other gases in the atmosphere are very inactive, their presence is not harmful for most of the purposes for which the nitrogen is desired. Such nitrogen is known as *atmospheric nitrogen.*

We are next going to describe how nitrogen is prepared from chemicals and to do this we will have to call the substances by their chemical names. These names are derived from the

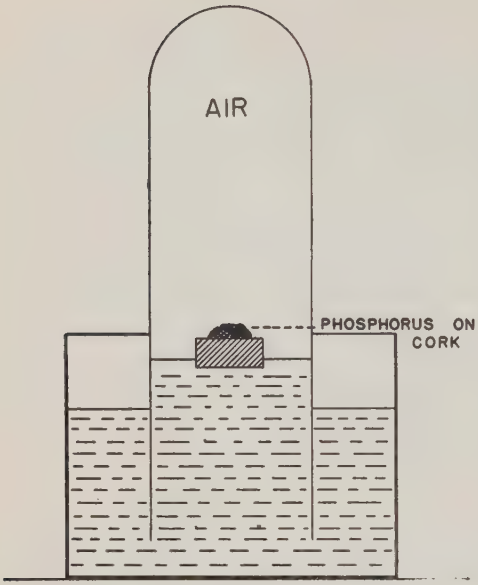


Fig. 21. Removing oxygen from the air by phosphorus leaves atmospheric nitrogen in the tube.

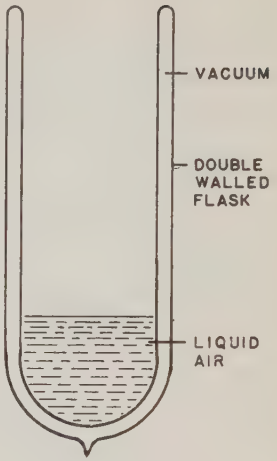


Fig. 22. Dewar flask in which liquid air will boil slowly. Nitrogen boils off first leaving liquid oxygen.

composition of each compound. In order to give you an idea of what elements go to make up these strange substances the so-called formula is also given. In these formulas each element is represented by a symbol which is a capital letter, or a capital letter and a small letter. The number of times the element occurs in a certain part of the compound, or in the smallest unit of the substance, is indicated by a small numeral after the symbol. The table of elements at the end of this book will show you the meaning of each symbol.

(2) *By the heating of ammonium nitrite.* Pure nitrogen may be prepared by heating ammonium nitrite, NH_4NO_2.

Ammonium nitrite yields nitrogen and water.

$$NH_4NO_2 \longrightarrow N_2 + 2\ H_2O$$

Ammonium nitrite is very unstable and is apt to explode when heated so the reaction is carried out by heating a mix-

ture of ammonium chloride and sodium nitrite. This mixture produces ammonium nitrite which decomposes as fast as it is produced.

Ammonium chloride + sodium nitrite ⟶ ammonium nitrite + sodium chloride.

$$NH_4Cl + NaNO_2 \longrightarrow NH_4NO_2 + NaCl$$

The apparatus for this laboratory method is arranged as shown in Fig. 23, and the gas is collected in a pneumatic trough.

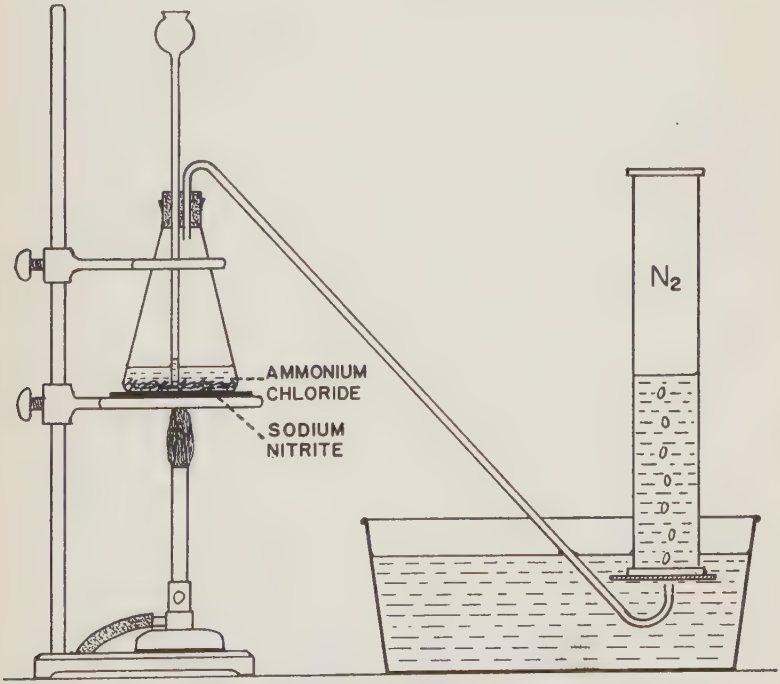


Fig. 23. Preparation of pure nitrogen from ammonium nitrite.

(3) *By passing ammonia over copper oxide.* Pure nitrogen may also be prepared by passing ammonia gas over heated copper oxide.

Copper oxide and ammonia yield water, copper and nitrogen.

$$3\ CuO + 2\ NH_3 \longrightarrow 3\ H_2O + 3\ Cu + N_2$$

B. Industrial Method. *From liquid air.* In the production of oxygen from liquid air the nitrogen is allowed to boil off, leaving the oxygen. If desired, this nitrogen may be collected and compressed into cylinders for industrial use. The nitrogen is not pure but the presence of small quantities of inert gases will not be harmful for most purposes for which the gas is required. This is a physical change so there is no chemical equation.

9. Properties of nitrogen.

A. Physical Properties. Nitrogen is a colourless, odourless and tasteless gas which is slightly soluble in water. Liquid nitrogen boils at $-196°C$. and freezes at $-210°C$. The gas is slightly less dense than air.

B. Chemical Properties. Nitrogen is a very inactive element and does not enter into many chemical reactions. It will unite with a few elements under certain conditions and such processes are known as the *fixation of nitrogen.* The gas forms five oxides but most of them are formed indirectly and not by a direct union of the elements. Nitrogen unites with a few of the metals to form *nitrides*, of which the most common are those of calcium, magnesium and aluminum. These nitrides will decompose when treated with steam, and this process can be considered as a method of fixing nitrogen although it has no practical value. Since nitrogen is so inert most of its compounds are unstable and many of them find uses as explosives. Some of these compounds are very sensitive to shock. Nitrogen is considered to be one of the most valuable elements in industry because of the extensive use of its compounds.

10. Uses of nitrogen. Nitrogen is used generally in the form of its compounds, such as ammonia and nitric acid, in the manufacture of fertilizers, dyes and explosives. It is used in the manufacture of incandescent electric lamps and in mercury thermometers which are used for high tempera-

tures, since the presence of the nitrogen reduces the tendency of the metal to evaporate.

11. The discovery and preparation of the lazy gases. Among the constituents of the atmosphere is a group of gases which will not react with any of the other elements. For this reason we shall call them the "lazy gases" but they are usually known as the *inert gases*. When you study the classification of the elements you will find that these gases occupy Group 0 of the Periodic Table (see Chap. 30). In 1785, Cavendish found evidence of the presence of these gases in the atmosphere, but he did not realize the significance of his discovery. In 1894, Lord Rayleigh was comparing the densities of samples of nitrogen, which he had prepared from the air, with the densities of other samples of nitrogen, which had been prepared by chemical means. He found that the nitrogen made from air weighed more per litre than that prepared by chemical means and he concluded that the explanation was due to the presence of another gas in the air, which was denser than nitrogen, and which, like nitrogen, was inactive. Rayleigh and Ramsay found a portion of the air which would not combine with magnesium to form a nitride and they named this element *argon* (lazy), because of its inertness.

In 1868, Janssen found a line in the spectrum of the sun which could not be ascribed to any element then known. Lockyer concluded that this was an element which existed on the sun and not on the earth, and he gave it the name *helium* (sun). In 1889, Hillebrand discovered an inert gas in a mineral and Ramsay identified this gas as helium in 1894. Helium was later discovered in natural gas in Texas, and it is now prepared in large quantities in a plant built by the United States government.

In 1898, *neon* (new); *krypton* (hidden); and *xenon* (stranger) were obtained by the fractional distillation of liquid air by

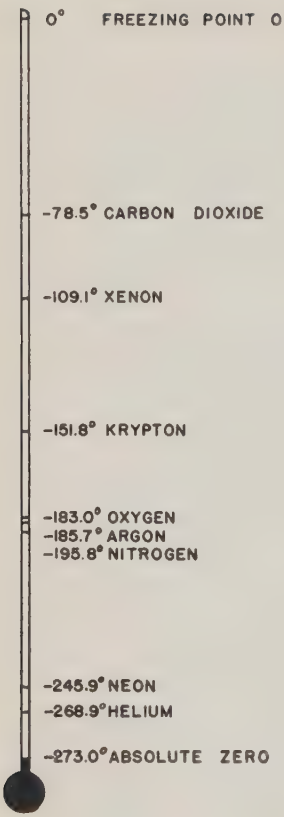
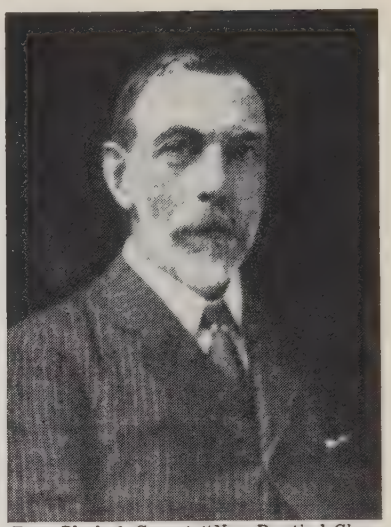


Fig. 24. The boiling points of the gases in the air.



From Black & Conant: "New Practical Chemistry," courtesy of The Macmillan Company.

Fig. 25. Sir William Ramsay (1852-1916), an English chemist who discovered many of the rare gases.

Ramsay and Travers. If a mixture of liquids is allowed to boil, the separate constituents boil off at different temperatures. If care is used, the constituents may be separated completely from one another, even though their boiling points are quite close together. This process is known as *fractional distillation* and is used in many industrial processes, such as the separation of the different hydrocarbons in petroleum (see Chap. 43). In Fig. 24 is a diagram showing the relative boiling points of the constituents of liquid air, in which it will be seen that the different gases have boiling points lying between absolute zero and the freezing point of water.

12. Uses of the inert gases. For many years hydrogen has been used in balloons because of its extreme lightness, but since it is very flammable there is a great danger of fire. Helium has almost as good a lifting power as hydrogen and possesses the great advantage of being non-flammable. Shortly after the first World War many nations experimented with dirigible balloons and many serious accidents occurred with hydrogen-filled aircraft. Since helium production was controlled by the United States government it was not available to all the nations for use in dirigibles and many turned their attention to heavier-than-air machines. Helium-filled dirigibles were used by the United States in World War II in their off-shore search for submarines, but they are not now used generally.

When men work in caissons, diving bells, or in diving suits under high pressure, the nitrogen of the air tends to dissolve in the blood. When the men come into an atmosphere of lower pressure, the nitrogen comes out of solution and forms bubbles in the blood vessels which cause cramps known as *bends*. It is found that when helium is used instead of nitrogen to dilute the oxygen used for breathing under these circumstances the tendency towards the production of bends is reduced.

Argon is used to fill incandescent electric light bulbs, for which purpose it has been found to be better than nitrogen. The bulbs are evacuated in order to get rid of the oxygen which would cause rapid oxidation at the temperature of the filament, but in the evacuated space the particles of metal will distill towards the cold wall of the bulb. If an inert gas is introduced into the bulb the increased pressure which can be used reduces the tendency to evaporate.

Neon is used in the "neon signs" which are now such a familiar sight. A high-voltage electric current is passed through the gas in the tubes, which then emits energy in the

form of light. In addition to their advertising use, these tubes are useful as beacons for ships and aircraft, as their colour has great penetrating power through fog.

Krypton and xenon have no commercial value at present and are available only in very small quantities, but a use may be found for them in the future. The story of these gases is an interesting one, since they are available in such small quantities and are useful for their physical properties alone. Since their chemical inertness prevents them from combining with any other elements they may well be called the "lazy gases".

13. Some other constituents of the atmosphere. Hydrogen is present in the atmosphere in such small quantities that there is no economic value in its extraction, as it can be obtained much more cheaply in other ways. In the portion of the atmosphere which is known to man the amount of hydrogen is so minute that it may as well be thought of as not being there at all and it is often omitted from a list of the gases of the atmosphere.

Carbon dioxide is an important constituent of the atmosphere although it is present in small quantities only. It is produced by the respiration of all plants and animals and by the combustion of our fuels, so you would expect that there would be large quantities of it in the atmosphere at all times. It is removed from the atmosphere by green plants which use it for their growth. Green plants have the property of converting carbon dioxide and water into cellulose or plant tissue, and they maintain a balance such that there is only about 0.03 per cent present in the atmosphere.

Because of the presence of water on the surface of the earth there will be water vapour in the air. This water vapour will possess a pressure which is dependent on the temperature. The quantity of water vapour in the air will therefore vary in different localities according to the temperature.

The amount of water present in the air as vapour is known as the *humidity*. As in the case of a solute dissolved in a solvent, there will be a temperature where the air will be saturated with water and the humidity will be at a maximum. The humidity can be expressed in milligrams per litre or grains per cubic foot, but it is usual to express the amount of water present as a percentage of the greatest amount that it would be possible to have at that particular temperature. This percentage is known as the *relative humidity*. If the air is completely dry the relative humidity is 0 per cent, and if the air is saturated with water vapour, the relative humidity is 100 per cent. The water vapour content of the atmosphere varies from day to day and from hour to hour.

14. Conditioning the atmosphere. The comfort of the human body depends upon its ability to maintain an even temperature. If the body gets too hot, water is discharged from the pores as perspiration and the evaporation of this water from the skin will cool the body. If the air is so full of water vapour that it cannot take any more, the perspiration will not evaporate and the body will feel hot and uncomfortable. If the air is very dry there will be a very rapid evaporation of perspiration which will result in a cracking of the skin and an excess cooling effect. Modern air conditioning seeks to control both the temperature and the humidity. It has been found that the human body is most comfortable when the humidity is around 40 per cent and arrangements are made to maintain the proper quantity of water vapour in the air so as to obtain the most comfort. If the air is too moist, water vapour can be removed; and if it is too dry, water vapour can be added. Air conditioning has done much for the comfort of man and has enabled him to carry on work where it would otherwise be unbearable. It has been said that everyone complained about the weather but nobody did anything about it. It is now possible to do something.

Question Summary

1. Name some of the "airs" known to early experimenters.

2. (*a*) Give the approximate composition of dry air.
(*b*) Name some substances that may be in the air because of local conditions.

3. Name as many facts as you can to show that air is a mixture. Which seems to you to be the most reasonable?

4. (*a*) What is meant by critical temperature?
(*b*) Describe the method of making liquid air.
(*c*) Name some other gases besides air which are used in the liquid state.

5. Describe the discovery of nitrogen.

6. (*a*) How does nitrogen occur on the earth?
(*b*) Why is nitrogen of economic importance?

7. Describe the nitrogen cycle.

8. (*a*) Describe a laboratory method of preparing nitrogen from atmospheric air.
(*b*) Describe a method of preparing nitrogen from chemicals available in a laboratory.
(*c*) What is the industrial method of obtaining nitrogen?

9. (*a*) Give the physical properties of nitrogen.
(*b*) Describe the chemical properties of nitrogen.
(*c*) What are nitrides?

10. Name some of the uses of nitrogen.

11. (*a*) Describe the discovery of argon.
(*b*) What is meant by fractional distillation?
(*c*) Describe the discovery of helium.

12. Give the uses of the inert gases.

13. (*a*) Why is carbon dioxide an important constituent of the atmosphere?
(*b*) What is humidity? What is relative humidity?

14. (*a*) What effect does the water vapour in the atmosphere have on the comfort of the human body?
(*b*) Describe the principle of air conditioning.

Problems for Review

1. How many grams of ammonium nitrite would be required to produce 56 grams of nitrogen?

2. How many grams of nitrogen would you get by passing 150 grams of ammonia over cupric oxide?

3. What volume of nitrogen at S.T.P. would you get from 500 grams of ammonium nitrite?

4. How many grams of cupric oxide would be required to react with ammonia in order to obtain 200 litres of nitrogen at S.T.P.?

5. How many litres of nitrogen at S.T.P. would you obtain by passing 10 litres of ammonia at 300°C. and 1000 mm. over cupric oxide?

Chapter 5

Oxygen and Ozone

1. Introduction. You have learned that oxygen was discovered by Scheele in the search for the nature of fire. Unfortunately Scheele did not publish his work until several years had passed and the credit for the discovery has been given to Joseph Priestley, an English clergyman, who prepared oxygen by heating mercuric oxide. Priestley performed several experiments with oxygen and found that it supported combustion. He decided to try its effect on small animals and placed two mice inside a jar containing the gas. He observed that the mice appeared to suffer no discomfort and he tried the effect of breathing it himself. In his report to the Royal Society, which he made in 1775, he remarked, ". . . The feeling of it to my lungs was not sensibly different from that of common air, but I fancied that my breast felt peculiarly light and easy for some time afterwards. Who can tell but that in time this pure air may become a fashionable article of luxury? Hitherto only two mice and myself have had the privilege of breathing it." It is interesting to see how Priestley foretold one of the most valuable uses of the gas.

2. Occurrence. Oxygen is found in the free state in the atmosphere to an amount of about 20 per cent. In the combined state it is found in water, in rocks, in vegetation and in the bodies of animals. It is the most plentiful element on the earth and about 50 per cent of the earth's crust consists of oxygen. Since oxygen comprises eight-ninths of the weight of water, you can realize how many tons of oxygen there

must be in the ocean. More than 60 per cent of the weight of your own body is due to oxygen. In addition to entering into the composition of the bodies of all animals, it is essential for the existence of both plant and animal life on the earth through respiration.

3. Laboratory methods of preparing oxygen.

(1) *The heating of mercuric oxide.* Oxygen may be prepared in the laboratory by heating certain metallic oxides. Compounds consisting of oxygen and another element are known as *oxides.* In the classical experiment of Priestley, mercuric oxide was heated and the oxygen was obtained. The yield is too small and the oxide is too expensive to allow this method to be of much value as a source of oxygen. The equation for the *decomposition*, or breaking up, of mercuric oxide is:

Mercuric oxide yields mercury and oxygen.

$$2\ HgO \longrightarrow 2\ Hg + O_2$$

This method is not a general one which can be applied to all oxides as some will not decompose when heated, while others will explode when warmed slightly. Among the oxides which yield at least a portion of their oxygen when heated are barium peroxide, BaO_2, red lead oxide, Pb_3O_4, and silver oxide, Ag_2O.

(2) *The heating of potassium chlorate.* Some compounds containing oxygen together with other elements will give off a part or all of their oxygen when they are heated. When potassium chlorate, $KClO_3$, is heated to a temperature above its melting point, 368°C., oxygen is set free and a white solid, potassium chloride, KCl, is left. At temperatures below the melting point of potassium chlorate some decomposition does occur but the reaction is so slow that it is of little value. If a little manganese dioxide, MnO_2 or ferric oxide, Fe_2O_3, is mixed with the potassium chlorate, the

reaction will proceed more rapidly at a much lower temperature (about 200°C.). The oxygen does not come from the manganese dioxide or ferric oxide, since they can be heated to this temperature without decomposition. It is found also that these substances can be recovered after the reaction is completed and that their weight is unchanged by the process. Apparently these substances possess the property of allowing the reaction to proceed at a lower temperature while they themselves are not affected. *Any substance that changes the speed of a chemical reaction while not undergoing any chemical change itself*, so that it may be recovered unchanged when the reaction is completed, is known as a *catalyst*. The use of such a substance is called *catalysis*. You will find that catalysts play an important part in many industrial processes.

The equation for the decomposition of potassium chlorate is as follows:

Potassium chlorate yields potassium chloride and oxygen.

$$2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2$$

You will notice that the catalyst is not included in the equation. A chemical equation shows all the substances that enter into the chemical change, but does not include those substances that may be present but do not undergo any permanent chemical change.

The apparatus for the preparation of oxygen by heating potassium chlorate is shown in Fig. 26. The potassium chlorate and the catalyst are mixed together and placed in the tube. Either manganese dioxide or ferric oxide may be used as a catalyst. Manganese dioxide causes very rapid action and the use of ferric oxide allows greater control of the evolution of the gas. The gas is usually collected over water in a *pneumatic trough*. The collecting jars are filled completely with water, inverted in the trough, and placed over the end

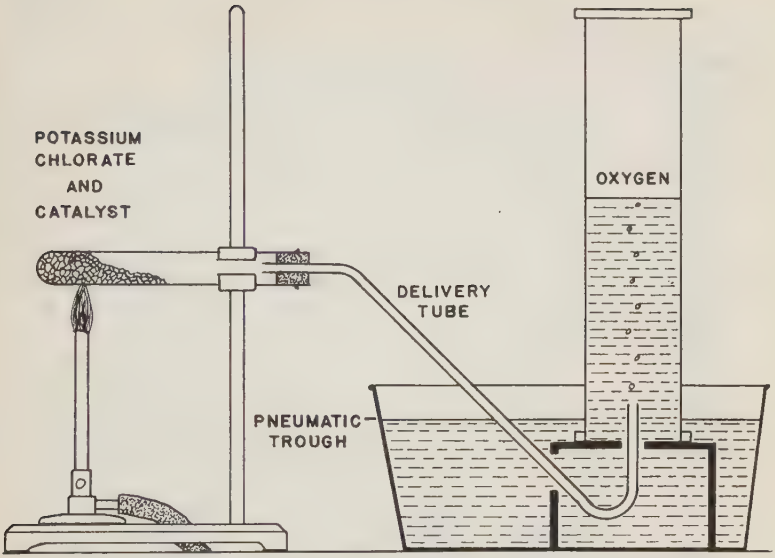


Fig. 26. Preparation of oxygen by heating potassium chlorate.

of the delivery tube when they are to be filled with the gas. When the generating tube is heated gently a gas is evolved. The first bubbles consist of air and are neglected, but in a short time the flow of gas increases and oxygen is given off. Although oxygen is colourless, the gas in the jar may appear cloudy because of fine particles of solid material carried over with the gas. Upon completion of the experiment the catalyst may be separated from the potassium chloride by placing the material left in the tube in water, which is afterwards passed through a filter. The potassium chloride is soluble in water and will pass through the filter, but the catalyst is not soluble and will remain on the filter paper.

(3) *The action of water upon sodium peroxide.* When cold water is allowed to drop upon sodium peroxide, Na_2O_2, oxygen is evolved and sodium hydroxide is produced. If the water is hot the action will take place with explosive violence. This reaction may be carried out in the laboratory

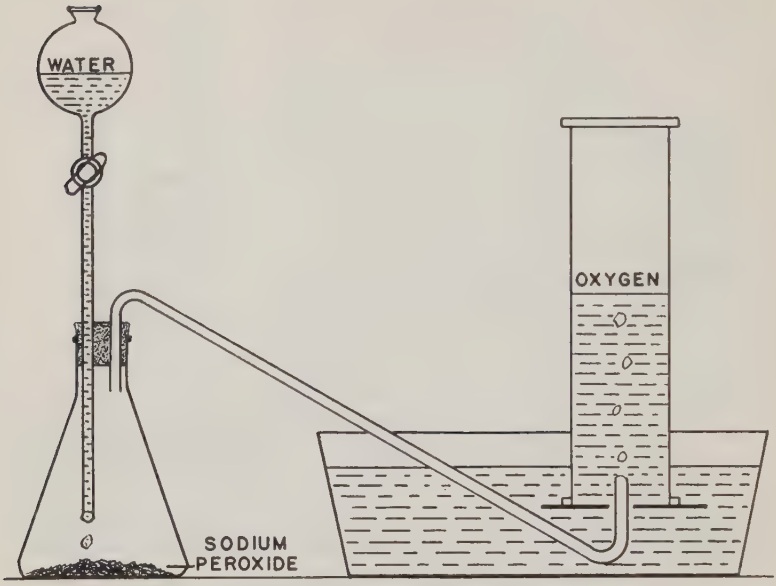


Fig. 27. Preparation of oxygen from sodium peroxide.

in the apparatus shown in Fig. 27. The sodium peroxide is placed in the flask and water is allowed to drop upon it from the dropping funnel. The action is immediate and no heat is required. The gas may be collected in a pneumatic trough. This is a convenient way to produce small quantities of oxygen because the flow of gas can be regulated easily and no heat is required. The equation for this reaction is as follows:

Sodium peroxide and water yield sodium hydroxide and oxygen.

$$2\ Na_2O_2 + 2\ H_2O \longrightarrow 4\ NaOH + O_2$$

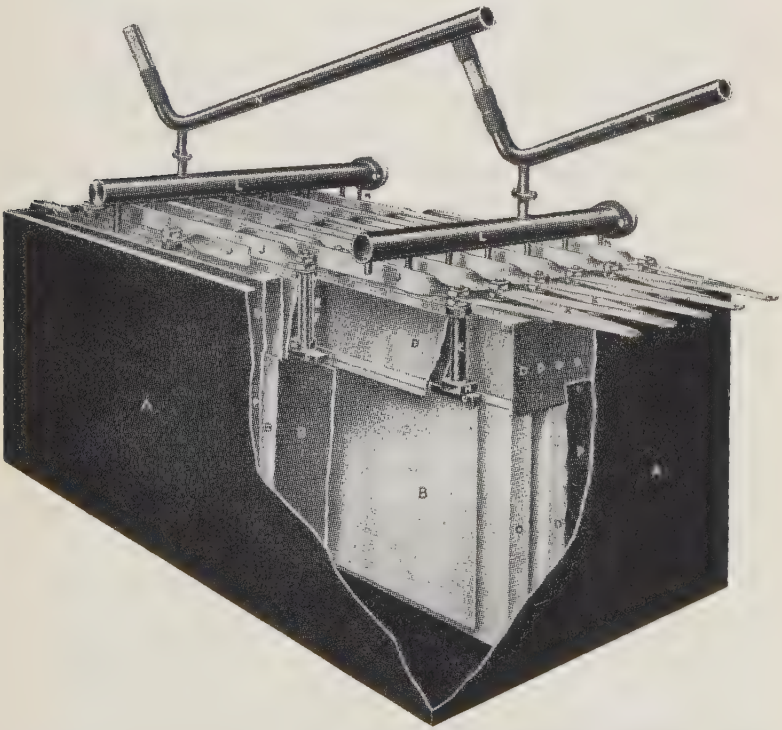
It will be seen from the equation that one-half of the oxygen in the sodium peroxide is obtained by this method, the other half being used in the production of the sodium hydroxide.

4. Industrial methods of preparing oxygen.

(1) *The preparation of oxygen from water.* Nicolson and Carlyle discovered as early as 1801 that water could be

"taken apart" by an electric current. This apparently simple substance is separated into two different elements, hydrogen and oxygen, by the passage of an electric current. The industrial apparatus, shown in Fig. 28, consists of pairs of inert metal plates called *electrodes*, on the ends of insulated leads carrying the current. The gases are collected in bells and taken off in pipes. Safety pipes, N, are provided in case the main leads become blocked. The plates are separated by asbestos diaphrams which prevent the mixing of the liberated gases.

The plate connected to the positive lead is the *anode* and the oxygen gas arises from this anode. The negative lead



Courtesy The International Electrolytic Plant Co.

Fig. 28. Knowles cell for producing oxygen and hydrogen by electrolysis.

is attached to the *cathode*, where the hydrogen collects. A little of an acid, base, or salt will make the water a conductor of electricity so these substances are called *electrolytes*. Sodium hydroxide is usually used because it is not itself decomposed by the electric current when dissolved in water. If all sources of error are eliminated, the volume of hydrogen produced is just twice as great as the volume of oxygen.

Water yields hydrogen and oxygen.

$$2\ H_2O \longrightarrow 2\ H_2 + O_2$$

Much hydrogen and oxygen is prepared by electrolysis at Trail, B.C.

(2) *The preparation of oxygen from liquid air.* Nitrogen, which comprises about four-fifths of the air, boils at $-196°C.$, while oxygen boils at $-183°C.$ When liquid air evaporates, the nitrogen will thus boil away first, leaving a residue of almost pure oxygen. The oxygen may be allowed to evaporate and the gas compressed in the steel cylinders in which it is commonly sold. Since this process is a physical change it is not represented by an equation.

5. Properties of oxygen.

A. *Physical properties.* At room temperature oxygen is a colourless, odourless and tasteless gas which is slightly soluble in water. It is the oxygen which is dissolved in the water (not the oxygen which is a constituent of the water) that is used by fish in their respiration. Oxygen is 1.1 times as heavy as air, and one litre at 0°C. and 760 mm. mercury pressure, weighs 1.429 g.

B. *Chemical properties.* At low temperatures oxygen does not combine with many substances, but at high temperatures it combines directly with many of the elements. It does not combine directly with nitrogen except at very high temperatures; however, there are several oxides of nitrogen which can be made indirectly. Oxygen does not combine with the

least active metals, such as gold, silver and platinum. The more active metals combine with the oxygen of the air and react more vigorously with pure oxygen to form basic oxides.

Sodium and oxygen yield sodium peroxide.

$$2\ Na + O_2 \longrightarrow Na_2O_2$$

Calcium and oxygen yield calcium oxide (quicklime).

$$2\ Ca + O_2 \longrightarrow 2\ CaO$$

Iron and oxygen yield iron oxide.

$$3\ Fe + 2\ O_2 \longrightarrow Fe_3O_4$$

The slow combination of iron with oxygen is known as *rusting*. The combination of any substance with oxygen is known as *oxidation*. If heat and light are given out it is usually referred to as *burning* or *combustion*. You must remember, however, that the rusting of iron, the burning of paper or coal, the decay of wood, and all processes which involve a combination with oxygen are forms of oxidation, whether they proceed rapidly or slowly and whether or not heat and light are produced.

When the oxides of some metals react with water they form *hydroxides* which act as bases. Such oxides are called *basic oxides*. Bases react with acids to produce salts. Hydroxides that dissolve in water are known as *alkalis* and their solution is said to be *alkaline*. An alkaline solution may be tested by placing a drop of it on a piece of *red* litmus paper. If the solution is alkaline the red litmus paper will turn *blue*. You can remember this by the word **BARB**: **B** is for base, **A** is for turn, **R** is for red litmus, **B** is for blue.

Sodium peroxide and water yield sodium hydroxide and oxygen.

$$2\ Na_2O_2 + 2\ H_2O \longrightarrow 4\ NaOH + O_2$$

Calcium oxide and water yield calcium hydroxide (slaked lime).

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Oxygen combines directly with many non-metals to produce acidic oxides as shown by the following reactions:

Carbon and oxygen yield carbon dioxide.

$$C + O_2 \longrightarrow CO_2$$

Sulphur and oxygen yield sulphur dioxide.

$$S + O_2 \longrightarrow SO_2$$

Phosphorus and oxygen yield phosphorus pentoxide.

$$4\ P + 5\ O_2 \longrightarrow 2\ P_2O_5$$

You will remember that the oxides of non-metals react with water to form acids. Solutions of acids may be tested by dipping into them a piece of *blue* litmus paper. In an acid solution blue litmus paper will turn *red*.

Carbon dioxide and water yield carbonic acid.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

Sulphur dioxide and water yield sulphurous acid.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

Oxygen will also combine with many compounds. The compounds of carbon and hydrogen, known as *hydrocarbons*, and those of carbon, hydrogen, and oxygen, known as *carbohydrates*, are the most familiar. Our fuel oils are mainly mixtures of hydrocarbons, and the nature of their oxidation may be illustrated by considering the combustion of acetylene, C_2H_2. If both the carbon and the hydrogen would combine with the maximum amount of oxygen, carbon dioxide and water would be produced. The equation would read.

Acetylene plus oxygen yields carbon dioxide and water.

$$2\ C_2H_2 + 5\ O_2 \longrightarrow 4\ CO_2 + 2\ H_2O$$

This would represent the complete combustion of acetylene. The complete combustion of any compound of hydrogen and

carbon will give water and carbon dioxide as two of the products.

The combustion of such substances is often incomplete. When acetylene issues into the air it will burn if the temperature is over about 420°C., but the flame is very smoky and luminous because the acetylene is decomposed by the heat into carbon and hydrogen. The unburned carbon is the smoke and its incandescent particles in the burning gases give out light. If a stream of oxygen is mixed with the acetylene as in an oxy-acetylene torch (Fig. 29), the temperature becomes very high and the carbon is all burned. The

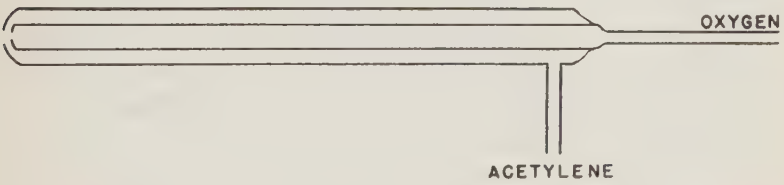


Fig. 29. Blow-pipe for burning gases with oxygen.

temperature rises to over 3100°C. At this temperature carbon monoxide is stable and water is decomposed into its elements. The acetylene burns with much less oxygen than that required for complete combustion, only about 1.5 volumes of oxygen being supplied for each volume of acetylene.

Acetylene plus oxygen yields carbon monoxide and hydrogen.

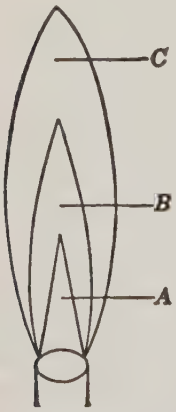
$$C_2H_2 + O_2 \longrightarrow 2\ CO + H_2$$

This reaction occurs in the zone of the flame; it is very important in the welding of metals because the hydrogen and carbon monoxide are reducing agents which keep the metal from burning up in the oxygen. As the temperature falls in the outer regions of the flame these gases burn in the excess oxygen of the air.

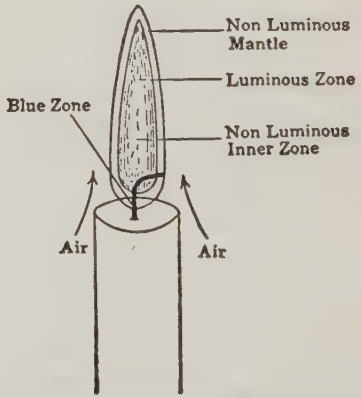
In cutting iron or steel a special inner tube in the oxy-acetylene torch directs a sharp jet of pure oxygen onto the

heated metal. The hot iron then burns brilliantly, emitting showers of sparks, and a very clean cut is produced. Plates over a foot thick can be cut with such a cutting torch.

The union of oxygen with carbohydrates is found in the burning of wood, paper and all materials containing cellulose $(C_6H_{10}O_5)x$. The animal oils and fats are also compounds of carbon, hydrogen and oxygen, and are oxidized to carbon dioxide and water. In burning oil with a wick, or gas from a jet, the structure of the *flame* is very characteristic. It consists of an inner cone where the oil is being vaporized or the gas heated to the ignition temperature, then a primary combustion zone where decomposition of the fuel and luminosity may occur and finally an outer zone where oxygen is abundant and the combustion is completed. Another zone of complete combustion exists near the outside of the base of the flame called the blue zone. These zones are shown in Fig. 30.



From Holmes: "General Chemistry", courtesy of The Macmillan Company.



From Conant: "Organic Chemistry", courtesy of The Macmillan Company.

Fig. 30. Zones in the flames of a bunsen burner and a candle.

When a bunsen burner has the air ports open enough to give an excess of air to the inner cone the luminous zone will

disappear. The luminous part is due to carbon particles which remain unburned long enough to be heated to incandescence and when excess air is available to gaseous fuels the flame is almost invisible. An alcohol lamp flame is very hard to detect in bright sunlight.

6. Uses of oxygen. Oxygen is used extensively in industry in the oxy-acetylene torch. The oxy-hydrogen torch is used for similar purposes. The medical profession uses oxygen in cases of pneumonia and asphyxiation. Oxygen is also used in mine rescue work, high-altitude flying, submarine operations, and in similar occasions where there is a limited amount of air for normal respiration. Liquid oxygen may be used with charcoal as an explosive which possesses certain advantages in that no injurious gases are produced on explosion, and unexploded charges are not dangerous as the liquid oxygen soon evaporates. Liquid oxygen is used as a portion of the fuel in modern rockets. The industrial use of oxygen is small compared with the use of the oxygen of the air. Oxygen is necessary for the existence of all plants and animals and for most of the heat of the world. Oxygen also acts as a natural cleanser as it oxidizes dead and decaying material, converting it into harmless substances.

The test for oxygen is to insert a glowing splinter into the gas. If the gas is oxygen the splinter will burst into flame but the gas itself will not burn.

7. Factors influencing the rate of combustion and other reactions.

(i) *Surface area or concentration.* Since combustion can only take place when the substance being burned comes in contact with the air, fine powders will burn more easily than large lumps because they present a larger surface to the air. Powdering the material is the same as increasing the concentration of an acid being used to dissolve a metal. If you put tin in hot, very dilute, hydrochloric acid you might

think it is insoluble but if you put it in concentrated acid you can see bubbles of hydrogen coming off. The same effect can be observed by putting a lump of tin in one tube of acid and finely powdered tin in another tube of the same acid. The effect is more quickly observed by putting a few millilitres of very dilute vinegar in one beaker and dropping in a one gram lump of washing soda while at the same time an equal amount of powdered washing soda is dropped into an equal volume of the same acid in another similar beaker.

(ii) *Temperature, and heat or light.* Coal will not burn in air unless its temperature is raised above room temperature. For every substance that will burn there is a certain temperature, known as the *kindling temperature* below which the substance will not burn.

In general, a rise in temperature increases the rate of a chemical reaction. In cases of slow oxidation, such as decay, the rate of oxidation also is accelerated by an increase in the temperature. Cold storage is based on the principle that the rate of decay is decreased by a decrease in temperature.

You have learned that heat is associated with all chemical changes. If a chemical reaction, such as oxidation, which gives out heat, proceeds in such a manner that this heat cannot escape but will remain to raise the temperature of the reacting substances, there is a possibility that the kindling temperature may be reached and that the substances will burst into flame. Such cases where fires start without any apparent agency are instances of *spontaneous combustion.* The best example of this, and one which might occur in a household, is when rags soaked in oil or paint are stored in a closed space. The oil in the paint oxidizes in the presence of the surrounding air and heat is produced. As the rags are in an enclosed space which prevents ventilating air currents and the cloth itself acts as an insulator to prevent the conduction of heat from the innermost layers, the heat produced by the

oxidation cannot escape. This pent-up heat raises the temperature of the pile of rags until the kindling temperature is reached and the whole mass bursts into flame. The fact that the oil has spread throughout the cloth has greatly increased the surface of the oil and that aids in the increase of the rate of oxidation. Under the conditions described there will be sufficient oxygen present to cause oxidation, though there is not enough freely-moving air to carry off the heat by convection currents. If the rags were tightly packed and completely enclosed there would not be sufficient oxygen to cause oxidation. Many fires of unknown origin may have been caused by such a simple thing as a pile of old rags in a closet. Large piles of coal have been known to commence burning because the innermost parts have oxidized and the pent-up heat has caused the temperature to rise and reach the kindling temperature. Coal must be piled in such a manner as to provide sufficient movement of air to carry off the heat that may be formed. There is, however, no danger in the small piles of coal kept in dwelling-houses.

(iii) *Catalysis.* You know that wet wood decays much more rapidly than dry wood. This is because moisture catalyses the oxidation of the cellulose in the wood. You have learned that certain finely divided oxides catalyse the decomposition of potassium chlorate and you will see many more examples of catalysis as you proceed.

In addition to concentration, temperature, and catalysis, we must remember that the chemical nature of the substances themselves play an important part in determining the rate of a reaction. These things are dealt with more fully in Chap. 16.

OZONE

8. Introduction. In 1775 van Marum observed a peculiar odour in the vicinity of electric machines in operation but

he made no attempt to find the cause. In 1840, Schönbein recognized that the odour was due to the formation of a substance to which he gave the name *ozone*, from the Greek "odour". The work of Andrews and Tait in 1860 showed that ozone was a form of oxygen.

This is the first case that you have met where an element can exist in different forms which may be distinguished from one another by their physical properties. The property of existing in different forms is known as *allotropy*, and the forms themselves are known as *allotropic forms*. Ozone is an allotropic form of oxygen and you will find several elements that exhibit this property. Sulphur, carbon and phosphorus are the best-known examples of elements which can exist in allotropic forms. To understand the essential difference between oxygen and ozone, you must be introduced to atoms, molecules, symbols and formulas.

Man now believes that all matter exists in the form of very small particles to which he has given the name *molecules* and that the molecules themselves are composed of still smaller particles known as *atoms*. You will learn later the fascinating story which tells how these conclusions were reached. For the moment we shall be content to define the molecule as the *smallest piece of matter that can have an independent existence* and the atom as *the smallest piece of an element that can enter into chemical combination to form molecules*. The elementary gases that you are now commencing to study possess molecules which contain two atoms. If you examine the chemical *symbols* which have been written in the chemical equations, you will see that we have written H_2 and O_2, which indicate the presence of two atoms, since each symbol stands for one atom, and each group of symbols, known as a *formula*, stands for one molecule.

While oxygen has two atoms in its molecule, which is written as O_2, ozone has three atoms so that its molecule

would be expressed by O_3. You can see by looking at this formula that ozone supplies more oxygen atoms for every molecule than does oxygen, and you will find that ozone acts like a more concentrated form of oxygen.

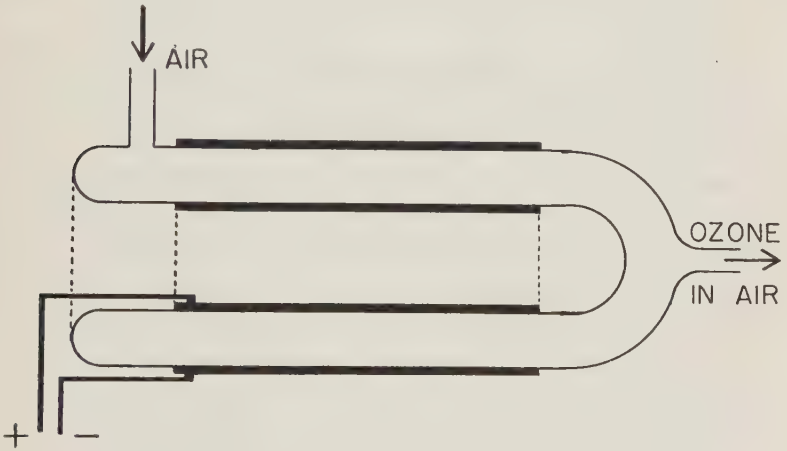


Fig. 31. Apparatus for converting oxygen to ozone. This is a longitudinal cross-section of the double-walled cylindrical glass flask which has metal electrodes inside and outside connected to a high voltage source.

9. Preparation and properties of ozone. Ozone is usually prepared by passing air through a glass vessel in which a silent electric discharge is taking place. A diagram of this apparatus is shown in Fig. 31. The vessel is shaped like a double-walled cylinder with circular electrodes placed around it. The discharge takes place through the walls of the vessel and the gas that is within. Only a small portion of the oxygen in the air passing through the vessel is converted into ozone, but some forms of ozonizing equipment will convert from 16 to 18 per cent of the oxygen into ozone. Better yields are obtained by using low temperatures and dry gas. By cooling with liquid air yields of 90 per cent may be obtained. Small quantities of ozone may be produced by lightning and the action of ultra-violet light upon oxygen in the upper parts

of the atmosphere; but in spite of the advertising claims of some summer resorts, there is not much ozone found in the atmosphere close to the earth. Some ozone is produced by electric sparks in the air and its odour may often be detected in the vicinity of electric motors or apparatus where sparks are produced.

The chemical properties of ozone are similar to those of oxygen except that ozone is more active. Some metals such as silver and gold, which are not tarnished by oxygen, are affected rapidly when exposed to ozone. Ozone decomposes to produce a molecule of oxygen and oxygen in the atomic form. When an element is released in the form of atoms it is apparently more active, and it is not liberated unless there is a substance present which can combine with it immediately. The atomic form of an element is sometimes referred to as the *nascent state*; you will learn more of this when you study the bleaching and disinfecting action of chlorine.

Ozone yields oxygen and atomic oxygen.

$$O_3 \longrightarrow O_2 + (O)$$

10. Uses of ozone. Air containing ozone has a number of uses that are based on the liberation of oxygen when the ozone decomposes. When ozone reacts with certain coloured substances it oxidizes them to colourless compounds, thus bleaching the material. A similar oxidation will render some bacteria harmless and thus bring about disinfection. In Europe, ozone is used to sterilize water and purify air, but its high cost renders its use limited. In America, chlorine is generally employed for these purposes.

Question Summary

1. (*a*) Who is credited with the discovery of oxygen?
   (*b*) How was oxygen first prepared?
   (*c*) What present-day use of oxygen did its discoverer foretell?

2. (*a*) Where is oxygen found on the earth?

(*b*) Name some substances containing oxygen.

3. (*a*) What is an oxide? Name a few.

(*b*) Give the word equation for the preparation of oxygen from an oxide.

(*c*) Describe the method of obtaining oxygen from potassium chlorate.

(*d*) What is a catalyst? How would you know if a substance was being used as a catalyst?

(*e*) Describe the method of obtaining oxygen from sodium peroxide.

4. (*a*) What distinguishes an industrial method from a laboratory method?

(*b*) Describe the industrial method of obtaining oxygen from water.

(*c*) Describe the industrial method of obtaining oxygen from air.

5. (*a*) Give the physical properties of oxygen.

(*b*) Describe the chemical properties of oxygen.

(*c*) Name some different types of oxidation and describe complete and incomplete combustion processes.

(*d*) Describe the reaction of metallic oxides with water. What is formed?

(*e*) Describe the reaction of non-metallic oxides with water. What is produced?

(*f*) You have a jar containing a gas which may be oxygen. Describe the test which you would employ.

6. Give some of the uses of oxygen.

7. (*a*) Describe the effect of exposed surface on the rate of oxidation.

(*b*) Describe the effect of temperature on the rate of reaction.

(*c*) How could a fire start in a pile of oily rags if they are kept in a cupboard?

8. (*a*) What is allotropy? Name some elements which exhibit this property.

(*b*) What is the difference between oxygen and ozone?

9. (*a*) Describe the preparation of ozone.

(*b*) What are the properties of ozone?

10. Give some uses of ozone.

Problems for Review

1. How many grams of oxygen will you get from 45 g. mercuric oxide?

2. How many grams of oxygen will you get from 488 g. potassium chlorate?

3. What volume of oxygen at S.T.P. will you get from 1000 g. potassium chlorate?

4. Assuming complete decomposition, what volumes of oxygen and hydrogen at S.T.P. would you get from 1 litre of water?

5. Assuming 100 per cent yield, what volume of ozone would you get from 50 litres of oxygen at S.T.P.?

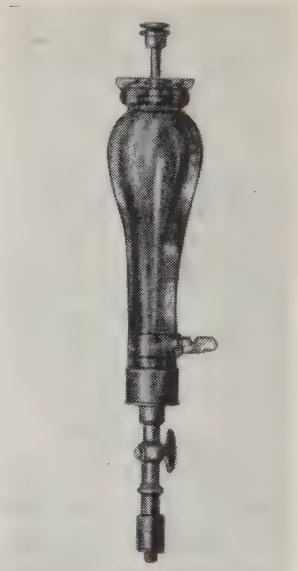
Chapter 6

Hydrogen

1. Introduction. It was known for a long time that a gas was produced by the action of acids upon metals. The famous Paracelsus, in the sixteenth century, observed the action between iron and sulphuric acid and stated quaintly that, ". . . an air arises which bursts forth like the wind". Van Helmont prepared this gas and observed that it would burn but would not support combustion. In 1766 Henry Cavendish described his experiments with hydrogen and carbon monoxide and stressed the individuality of the two gases. This was an important advancement in the study of gases at a time when the idea prevailed that almost all gases were identical with ordinary air. Cavendish called hydrogen "inflammable air" and both he and Priestley believed that it was phlogiston. Warltire had noticed that when hydrogen was exploded with ordinary air a dew was formed but he paid no attention to the nature of this liquid. Cavendish examined the liquid and found that it was water, formed presumably by the union of hydrogen and oxygen. He repeated the experiment using pure oxygen instead of air and found this to be true. He did not publish his results until 1784, and in the meantime Lavoisier performed the same experiments and claimed to be the discoverer of the composition of water. For many years a battle was waged between the admirers of Cavendish and those of Lavoisier, but the credit for the discovery is now given to the famous English scientist although it was Lavoisier who gave the name *hydrogen* (water former), to the gas.

Courtesy Fisher Scientific Co.

Fig. 32.



From Partington: "Inorganic Chemistry", courtesy Macmillan & Company Limited. (Figure of a photo of what is believed to be the original apparatus in the University of Manchester.)

Fig. 33.

Fig. 32. Henry Cavendish (1731-1810), English scientific recluse who discovered hydrogen.

Fig. 33. Cavendish's firing globe or eudiometer.

2. Occurrence. Hydrogen does not occur in the free state on the earth. It is found in minute traces in the atmosphere in the vicinity of the earth's surface and it is believed that the upper layers consist of almost pure hydrogen. It appears in many of the stars and in the sun. During an eclipse of the sun flaming streamers of hydrogen may be seen extending many thousands of miles into space.

Hydrogen is abundant in the combined state, although it comprises only a small percentage of the weight of the earth's crust because of its extreme lightness. It comprises one-ninth of the weight of water. Hydrogen is found in combination with carbon in natural gas and petroleum. In combination

with carbon, oxygen and other elements, it is found in all living things, and you will find that it is one of the most important elements in the study of the compounds of carbon. Hydrogen is the essential element in all acids and it is present in all hydroxides.

3. Laboratory methods for preparing hydrogen.

A. From water.

(1) *By the action of metals.* If a piece of the light metal potassium is dropped into water it will act with the water immediately. During the reaction the metal will displace the hydrogen from the water and will combine with the oxygen and part of the hydrogen of the water to form potassium hydroxide.

Potassium and water yield potassium hydroxide and hydrogen.

$$2\ K + 2\ H_2O \longrightarrow 2\ KOH + H_2$$

This is an example of a chemical reaction known as a *displacement*. If water be written in chemical symbols as HOH instead of H_2O it may be seen that the potassium displaces one-half of the hydrogen when it forms the compound potassium hydroxide. So much heat is liberated that when the hydrogen is produced it will catch fire and burn with a violet flame, the violet colour being due to the potassium. The action may be so violent that particles of potassium are thrown out of the vessel and the experiment must be performed carefully. The potassium hydroxide which is formed will dissolve in the water and a piece of red litmus paper dipped in the water will prove its presence by turning blue.

If sodium, which is a light metal like potassium, is used in this experiment a similar result will be obtained. The reaction is not quite so violent and the hydrogen does not usually catch fire. It may, however, be lighted, in which case it will burn with a yellow flame, the colour of the flame being due to the sodium. If the water is tested afterwards

with litmus paper it will show the presence of a hydroxide. The equation is similar to that showing the action of potassium on water.

Sodium and water yield sodium hydroxide and hydrogen.

$$2\ Na + 2\ H_2O \longrightarrow 2\ NaOH + H_2$$

The metal calcium will react also with water to produce hydrogen. The water becomes cloudy during the reaction, as the calcium hydroxide which is formed is not as soluble as either sodium or potassium hydroxide and does not all go into solution. Testing the solution with litmus paper shows that there is a hydroxide present. This reaction is not as violent as the others and the hydrogen can be collected if desired.

Calcium and water yield calcium hydroxide and hydrogen.

$$Ca + 2\ H_2O \longrightarrow Ca(OH)_2 + H_2$$

The metal magnesium will react with water to displace hydrogen if the water is heated.With cold water the reaction is too slow to be noticeable. Magnesium hydroxide is produced.

Magnesium and water yield magnesium hydroxide and hydrogen.

$$Mg + 2\ H_2O \longrightarrow Mg(OH)_2 + H_2$$

As you know, iron does not react with water under ordinary conditions to produce hydrogen, or we would not be able to use iron cooking utensils. However, if steam is passed over heated iron, hydrogen is given off and an oxide of iron is produced. The iron must be heated while the steam is passing over it or it will be cooled by the steam to a temperature which is too low to allow the reaction to proceed.

Iron and water yield iron oxide and hydrogen.

$$3\ Fe + 4\ H_2O \longrightarrow Fe_3O_4 + 4\ H_2$$

You will notice that an oxide of iron is produced instead of an hydroxide as in the previous cases of the action of a metal on water.

(2) *By electrolysis.* Hydrogen may be obtained from water at the same time as oxygen is liberated by electrolysis. A simple form of electrolysis apparatus useful for studying the process is shown in Fig. 34. The reaction of electrolysis may be expressed by the equation:

Water yields oxygen and hydrogen.

$$2\ H_2O \longrightarrow O_2 + 2\ H_2$$

The sulphuric acid or sodium hydroxide which is added to make the water a conductor of electricity does not appear in the equation, as it is not consumed during the reaction. Since it does not influence the speed of the reaction it is not considered as a catalyst.

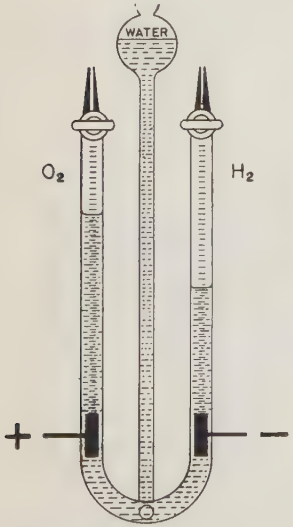
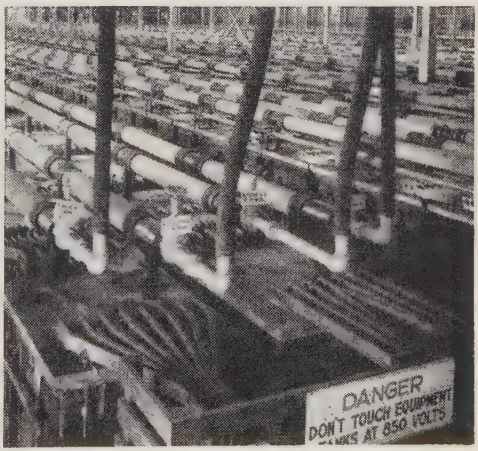


Fig. 34. Laboratory apparatus for the electrolysis of water.



Courtesy Consolidated Mining and Smelting Co.

Fig. 35. Large-scale production of hydrogen by electrolysis.

B. From acids.

The metals which displace hydrogen from water will also liberate it from acids, in which case a *salt* of the metal will be produced instead of the hydroxide. Some acids cannot be used for this reaction, as they will either not react noticeably or they will produce substances other than hydrogen. For example, nitric acid cannot be used as it will produce an oxide of nitrogen instead of hydrogen.

The common laboratory method of producing hydrogen is by using zinc and dilute sulphuric acid in the apparatus shown in Fig. 36, which consists of a flask fitted with a stopper carrying a thistle tube and a delivery tube which dips below the surface of water in a pneumatic trough.

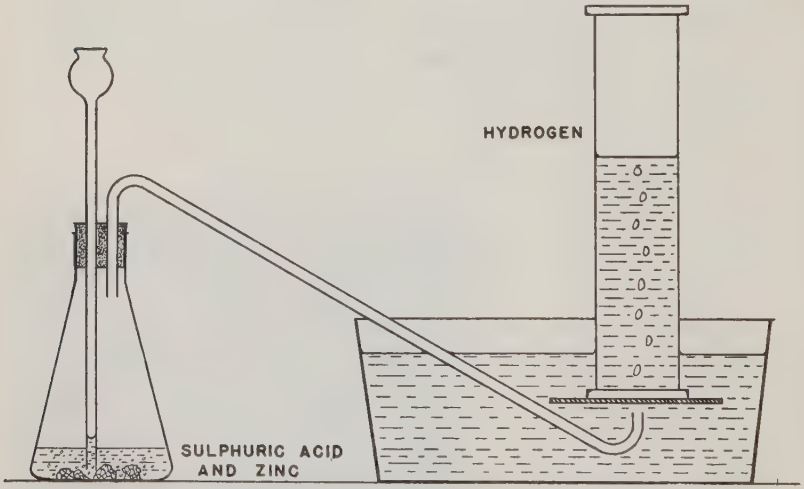


Fig. 36. Preparation of hydrogen by the dissolving of a metal in an acid.

The thistle tube is to enable more acid to be added during the experiment if it is needed; it also acts as a safety valve in case the pressure should rise. The end of the thistle tube must dip below the level of the liquid in the flask or the gas will pass out of it instead of the delivery tube. The gas is collected as in the case of oxygen by the downward displace-

ment of water. The zinc is placed in the flask and the apparatus assembled. As soon as the dilute sulphuric acid is added an action commences and the hydrogen is evolved without the addition of heat. The first bubbles to appear are air from the flask, but the hydrogen soon begins to appear in quantity and the collection of the gas may be commenced. The equation representing this reaction is:

Zinc and sulphuric acid yield zinc sulphate and hydrogen.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

The zinc sulphate is a white solid which belongs to the class of substances known as *salts*. It remains dissolved in the liquid in the flask. Dilute hydrochloric acid may be used instead of sulphuric acid, in which case zinc chloride will be formed instead of zinc sulphate and the reaction will be

Zinc and hydrochloric acid yield zinc chloride and hydrogen.

$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$$

Iron and tin may be used with either hydrochloric or sulphuric acid instead of zinc. In each case a salt of the metal will be produced as well as the hydrogen. The kind of salt will depend on both the metal and the kind of acid that is used.

4. Industrial methods of preparing hydrogen.

(1) *By electrolysis.* As you have seen, hydrogen may be obtained from water by electrolysis, oxygen being produced at the same time. This may be used as an industrial method if electricity is cheap enough.

When you study the element chlorine you will find that it may be prepared by the electrolysis of sodium chloride solution and that an equal volume of hydrogen is obtained at the same time. Hydrogen is thus a by-product in chlorine manufacture and this is an important industrial source of the gas.

(2) *From industrial gases containing hydrogen.* Hydrogen is present in coal gas, which is the gas we use in houses and in the laboratory for heating. It is produced by heating soft coal in the absence of air. The coal turns to coke and the gas is given off. This gas contains hydrogen which may be separated from the other constituents of the gas.

Water gas is prepared by passing steam through white-hot coke. The resulting gas contains carbon monoxide and hydrogen.

Carbon and water yield carbon monoxide and hydrogen.

$$C + H_2O \longrightarrow CO + H_2$$

Both water gas and coal gas are industrial sources of hydrogen.

5. Properties of hydrogen.

Physical properties. Hydrogen is a colourless, odourless and tasteless gas which is very slightly soluble in water. The gas can be liquefied and the liquid boils at $-235°C$. The most characteristic physical property of hydrogen is its extreme lightness. Under 760 mm. of mercury pressure at 0°C. one litre of the gas weighs only 0.0899 grams. It is the lightest of all the elements.

If gases are placed in vessels made of porous materials they will pass through the walls of the vessel. The passage of gases through substances is known as *diffusion* and the rate of diffusion is inversely proportional to the square root of the density. Being the lightest element, hydrogen will diffuse more rapidly than any other gas. The rate of diffusion also varies with the material through which the gas passes and with the pressure of the gas. Under high pressures hydrogen will even pass through steel walls at elevated temperatures.

Chemical properties. Hydrogen combines explosively with oxygen to form the oxide, *water*, when heated, but does not combine under ordinary conditions. The force of the

explosion is very great and it is dangerous to have lighted burners near hydrogen generators. Hydrogen also combines with oxygen to form hydrogen peroxide, H_2O_2. Hydrogen unites directly with many non-metals to form important compounds which will be studied in later chapters. With chlorine it forms hydrogen chloride; with sulphur, hydrogen sulphide; and with nitrogen it forms ammonia. Hydrogen combines with carbon to form hydrocarbons. Hydrogen also combines with a few of the metals to form substances known as *hydrides* which are unstable substances that react with water to liberate hydrogen and form the hydroxide of the metal. Sodium hydride, NaH, and calcium hydride, CaH_2, are examples of these substances.

The *test for hydrogen* is to place a lighted splinter to the mouth of an inverted jar of the gas. If the gas is hydrogen the flame of the splinter will be extinguished but the gas will burn with a pale blue flame, forming water which will collect as a mist on the inside of the jar. Some other gases will burn but hydrogen is the only gas that will produce water alone on burning.

6. Uses of hydrogen. Hydrogen is often burned with oxygen in the oxy-hydrogen blow-pipe which produces a very high temperature that is valuable for working metals. Its great affinity for oxygen allows hydrogen to remove that element from many substances. Many of the ores of metals are oxides and they may be converted to the metal itself by removal of the oxygen by hydrogen. This process is known as *reduction*. Hydrogen has an extensive industrial use in the preparation of ammonia and hydrocarbons. The preparation of solid fats by hydrogenation is of great importance because hydrogenated substances are used in the preparation of candles, soaps, margarine, and lard substitutes.

7. Reduction. The composition of water by weight may be determined by the apparatus shown in Fig. 37, in which

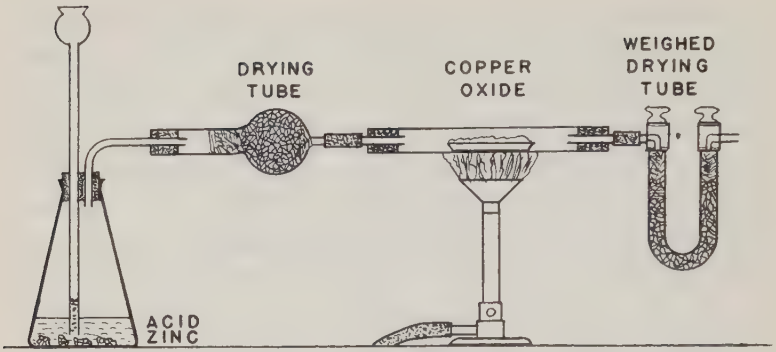


Fig. 37. Apparatus for finding the composition of water by weight.

dry hydrogen is passed over copper oxide. Any substance which has the power of removing oxygen from a compound is known as a *reducing agent.*

Hydrogen and copper oxide yield copper and water.

$$H_2 + CuO \longrightarrow Cu + H_2O$$

In this reaction the copper oxide acts as the oxidizing agent since it supplies oxygen, while the hydrogen acts as the reducing agent, since it combines with the oxygen and removes it from the copper oxide.

Hydrogen is not the only reducing agent, and you will find that carbon and carbon monoxide are used frequently in this capacity. A relatively low temperature will cause the reduction of copper oxide with carbon.

Carbon and copper oxide yield copper and carbon dioxide.

$$C + 2\ CuO \longrightarrow 2\ Cu + CO_2$$

It is seen that hydrogen is similar to carbon in that it removes oxygen from compounds by forming a more stable oxide than the one which is reduced by its action.

8. Composition of water. Lavoisier used the composition of water to prove the correctness of his oxygen theory of

combustion. After his day the composition of water was determined very exactly by two different methods.

(i) *Electrolysis* gave the composition by volume. In 1806 Sir Humphrey Davy showed that when very pure water is electrolyzed in a gold vessel and the experiment carried out in a vacuum to remove dissolved air from the water, the amounts of hydrogen and oxygen produced are really two volumes of hydrogen to exactly one volume of oxygen.

(ii) *Synthesis* gave the composition by volume or weight. The hydrogen may be made to combine in a eudiometer tube, see Fig. 38. This is a graduated tube with two platinum wires sealed through to make a spark gap similar to that in the cylinder of a motor-car engine. The eudiometer is filled with mercury and inverted in a dish of mercury. A stream of pure hydrogen is then allowed to bubble up and displace about 30 ml. of mercury. Then a stream of pure oxygen is allowed to displace one-half as large a volume of mercury in the tube. The spark gap is connected to an ignition system coil. When the spark is passed there is an explosion. The mercury falls and then rises as the water vapour condenses to a liquid. If there is exactly two volumes of hydrogen for each volume of oxygen the mercury nearly reaches the top of the tube.

This method enables us to determine the composition by volume but it is not convenient for finding the weights of the combining constituents. The great chemist Berzelius passed dry hydrogen over heated copper oxide and collected the water formed as the oxygen was removed from the copper oxide. He weighed the copper oxide before and after the reaction to determine the *weight of oxygen used*. By weighing the drying tube of calcium

Fig. 38. A simple explosion eudiometer.

chloride or phosphorous pentoxide before and after the reaction he found the weight of water produced from the oxygen. The difference in these two weights is the *weight of the hydrogen.*

Lavoisier's Law of Conservation of Weight is used in the latter calculation. Here are some figures to illustrate the method.

Weight of drying tube after the synthesis	= 36.260 g.
Weight of drying tube before the synthesis	= 35.366 g.
Weight of water synthesized	= 0.894 g.
Weight of copper oxide before reduction	= 8.425 g.
Weight of copper oxide after reduction	= 7.631 g.
Weight of oxygen used for synthesis	= 0.794 g.
Weight of hydrogen used for synthesis	= 0.100 g.

Thus one part by weight of hydrogen has combined with 7.94 parts by weight of oxygen to form water. This method is called a *gravimetric* synthesis because all the constituents are determined by weighing them on a balance.

The percentage composition can be found directly from these figures. The percentage of hydrogen is $\frac{.100}{.894} \times 100$, or 11.2 per cent. The percentage of oxygen is the remainder or 100 minus 11.2 which is 88.8 per cent. We usually say *water is* $\frac{1}{9}$ *hydrogen and* $\frac{8}{9}$ *oxygen by weight.* Water is thus a definite compound of hydrogen and oxygen. It could be called hydrogen oxide.

9. Another compound of hydrogen and oxygen. You have heard the term "peroxide blonde" and you know the solution used for bleaching and disinfecting is called hydrogen peroxide. This is a different compound of hydrogen and oxygen which contains twice as much oxygen combined with the same weight of hydrogen. It contains 15.88 parts of oxygen for each part by weight of hydrogen. Equal volumes of hydrogen and oxygen could be produced by the electrolysis

of the pure compound. The name contains the prefix "per" which means the compound contains more than the ordinary amount of oxygen.

Hydrogen peroxide is made industrially by two methods.

A. *Older method.* Cold dilute sulphuric acid reacts with a white oxide of barium called barium peroxide.

Barium peroxide + sulphuric acid ⟶ barium sulphate + hydrogen peroxide.

$$\mathbf{BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2}$$

Since barium sulphate is an insoluble white solid it can be removed from the liquids by filtration along with any unused barium peroxide. The filtrate is evaporated in a partial vacuum.

B. *Newer method.* Persulphuric acid yields hydrogen peroxide when it is distilled under reduced pressure.

10. Properties of hydrogen peroxide. The properties of hydrogen peroxide depend mainly on the readiness with which it gives up its extra oxygen. You have seen this taking place in a cut when it is decomposed by a substance in the tissues. It may not be very good as a germicide but it is very useful for expelling pus and removing clotted blood. You have felt it decomposing in your mouth when you have used it for a gargle.

Hydrogen peroxide ⟶ water + oxygen.

$$\mathbf{H_2O_2 \longrightarrow H_2O + (O)}$$

This new-born or nascent oxygen readily combines with bacteria and other substances. Hydrogen peroxide is thus an oxidizing agent since it can provide oxygen to other compounds and elements. The colour of many pigments is destroyed by oxidation so hydrogen peroxide may be used for bleaching silk, wool, feathers, hair, ivory and other coloured materials.

Pure hydrogen peroxide can be obtained as a colourless syrupy liquid but 3 per cent solutions containing a stabilizer to slow down the decomposition are sold in brown bottles which tend to shut out the light. Light accelerates its decomposition and as this solution gives off ten times its own volume of oxygen, the bottle must have a screw cap.

Question Summary

1. Describe the experimental work of Cavendish on hydrogen.

2. How does hydrogen occur on the earth?

3. (*a*) Describe a method of obtaining hydrogen from water by means of a metal.

(*b*) How could you show that a hydroxide is produced by the method that you have just mentioned?

(*c*) Describe the production of hydrogen by electrolysis.

(*d*) Describe the common laboratory method of producing hydrogen from an acid.

4. (*a*) Name an industrial method of producing hydrogen from water.

(*b*) How is water gas prepared? What gases does it contain?

5. (*a*) Describe the physical properties of hydrogen.

(*b*) What is the outstanding physical property of hydrogen?

(*c*) Describe the chemical properties of hydrogen.

(*d*) Why do we hydrogenate oils?

(*e*) Describe the test for hydrogen.

6. Name some uses for hydrogen.

7. (*a*) What is reduction? What is a reducing agent?

(*b*) Give a word equation which illustrates reduction.

8. (*a*) What is the percentage composition of water by volume? Describe two methods for its determination.

(*b*) How would you determine the percentage composition of water by weight?

9. How would you prepare hydrogen peroxide?

10. How is the decomposition of hydrogen peroxide used?

Problems for Review

1. What weight of hydrogen will you get from 250 grams of zinc when it reacts with hydrochloric acid?

2. How many grams of zinc sulphate will you obtain from 250 grams of zinc during the production of hydrogen by the reaction of sulphuric acid on the metal?

3. How much sulphuric acid 98% pure will be required to produce 120 grams of hydrogen?

4. What volume of hydrogen at S.T.P. will you obtain from 75 grams of zinc by the use of sulphuric acid?

5. What weight of hydrochloric acid 30% pure will be required to produce 112 litres of hydrogen at S.T.P.?

6. What volume of hydrochloric acid containing 36.5 per cent of hydrogen chloride by weight and having a density of 1.2 grams per millilitre will be required to dissolve 3269 grams of zinc?

7. How many litres of oxygen are required to burn (*i*) 100 l. of hydrogen; (*ii*) 1 g. of hydrogen; (*iii*) enough hydrogen to make 100 g. of water; (*iv*) enough hydrogen to make 18 ml. of liquid water at 4°C.?

8. If 20 ml. of hydrogen and 20 ml. of oxygen are exploded together find (*i*) What is the volume of the remaining gas if all measurements are made at 25°C. What is the gas in the tube? (*ii*) What would be the volume if all measurements were made at 130°C.? What gaseous substances make up this volume?

9. Calculate the percentage composition of hydrogen peroxide by weight.

Chapter 7

The General Behaviour of Gases

1. Introduction. The changes in the volume of any gas with temperature and pressure may be stated precisely by mathematical laws. Some people find it difficult to think as precisely as must be done to follow the operations of mathematics, and your teacher may wish you to learn more about simple gases before asking you to think accurately about their changes in volume. If you can discipline yourself to learn thoroughly a few simple laws about gases you can apply this knowledge to each new gas that you study. This is the easiest way to understand the mysteries of gaseous behaviour.

2. Boyle's Law. Robert Boyle applied the scientific method to the behaviour of that elusive and seemingly unreal form of matter known as a gas. He tried to show that it obeyed natural laws and his first study involved the manner in which a gas exerts a pressure when it is confined in a vessel at a constant temperature. The apparatus used in this experiment is shown in Fig. 39. Boyle trapped a *given mass* of gas in a tube by means of mercury at *room temperature* (20°C.). By adding mercury to the long tube the pressure of the gas in the short enclosed part of the tube was increased. The difference in the levels of the mercury gave a measure of the pressure, and the volume of the enclosed gas could be read by means of a scale. By changing the pressure on the gas in the tube Boyle could

(*i*) Observe the changes in volume caused by changes in pressure.
(*ii*) Record the pressure-volume data which he obtained.
(*iii*) Make a generalization for the case of one particular gas.

Courtesy Fisher Scientific Co.

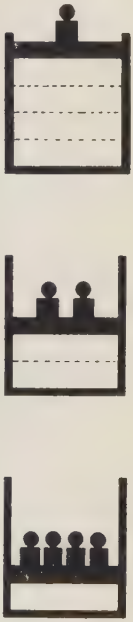


Fig. 39. **Fig. 40.** **Fig. 41.**

Fig. 39. Boyle's Law apparatus.

Fig. 40. Robert Boyle (1627-1691), an Irish scientist known as the "Father of Chemistry" because of his use of scientific method and his work on gases.

Fig. 41. Increasing the total pressure decreases the volume of a gas.

This was found to be a simple mathematical relationship. By using this method with other gases, the mathematical law has been found to be generally true for all reasonable pressures as long as the temperature of the gas is not too close to the temperature at which it will condense to a liquid.

Boyle's Law states that *for any given mass of gas at a constant temperature, the volume varies inversely as the pressure to which the gas is subjected.* This is shown in Fig. 41 and the following table.

TABLE 7—VARIATION OF THE VOLUME OF A GAS WITH PRESSURE

Case number	*Volume (V) in litres*	*Pressure (P) in atmospheres*	*Pressure × volume (PV) in litre-atmospheres*
1	100.0	0.1	10
2	50.0	0.2	10
3	20.0	0.5	10
4	10.0	1.0	10
5	5.0	2.0	10
6	2.0	5.0	10
7	1.0	10.0	10
8	0.5	20.0	10
9	0.2	50.0	10
10	0.1	100.0	10

The last column of the table shows that the product of the pressure and the volume is a constant quantity. We see that for each pressure-volume relation for this gas the product is the same. If we label the pressure and volume for case 1 as P_1 and V_1; those in case 2 as P_2 and V_2; and so on, we can then write

$$\mathbf{P_1V_1 = P_2V_2 = P_3V_3 = P_4V_4 \ldots\ldots\ldots = K_1}$$

We may measure the volume in any units, such as millilitres, cubic feet, cubic inches, etc., and we can measure the pressure in terms of pounds per square inch, tons per square foot, or in terms of the height of the liquid column which it will support, as centimetres of mercury, millimetres of mercury, feet of water, etc. As long as we use the *same units in each case* for a *given mass of gas* at a *constant temperature*, the product of the pressure and the volume will be constant.

3. Applications of Boyle's Law. The pressure-volume relation is used to compare the initial and final states of a gas. For example: if a given mass of gas has a volume of 300 cu. ft. under a pressure of 15 lb. per square inch, what volume will it have under a pressure of 60 lb. per square inch? You will notice that we are not using metric units in this problem, but that we are using the same units throughout. The work is done in two steps.

Step I. Arrange the initial and final states in tabular form.

	Pressure	*Volume*
Initial	15 (P_1)	300 (V_1)
Final	60 (P_2)	? (V_2)

Step II. Make the volume correction by Boyle's Law. This may be done by two methods.

Method A: The method of simple reasoning. Think! An increase in pressure, as on the downstroke of a pump, will squeeze the gas into a *smaller* volume. The new volume will be proportionally less than the initial volume. According to Boyle's Law it will be reduced by the ratio of the two pressures. To make the volume less the numerator must be less than the denominator. The new volume will be

$$300 \times \tfrac{15}{60} = 75 \text{ cu. ft.}$$

Method B: Substitution in a formula. In applying this method great care must be taken to distinguish which values are P_1, V_1, etc.

$$\text{If } P_1V_1 = P_2V_2, \text{ then } V_2 = \frac{P_1V_1}{P_2}, \text{ or } V_2 = \tfrac{15}{60} \times 300.$$

Therefore, V_2, as before, is 75 cu. ft.

The answer obtained by substitution in a formula should be checked by logical reasoning to assure yourself that it is plausible.

4. The Law of Charles. In 1801 John Dalton, an English schoolmaster, observed that gases expand by equal amounts due to equal changes in temperature. In 1802 Gay-Lussac pointed out that Charles had found this behaviour in 1787. Gay-Lussac measured the expansion accurately and stated a precise law.

"For a rise in temperature of 1°C. a given mass of gas at constant pressure expands 1/273 of its volume at 0°C."

The law is difficult to apply in this form, but a little reasoning will show how it may be made very simple.

If a gas *expands* 1/273 of its volume at 0°C. for each Centigrade degree *rise* in temperature, it will contract 1/273 of its volume at 0°C. for every Centigrade degree *fall* in temperature. Let us consider a gas that occupies a volume of 273 ml. at 0°C. If its temperature falls it will decrease its volume

by one millilitre for every degree drop in temperature. At −73°C. it will have a volume of 273 − 73 or 200 ml. At −173°C. it will have a volume of 273 − 173 or 100 ml. At −273°C. it would have a volume of 273 − 273, or no volume at all if it remained as a gas. Therefore −273°C. is a limiting value for temperature and it is impossible to imagine a temperature lower than that, since all matter must occupy some volume. This limiting temperature of −273°C. is known as *Absolute Zero.* See Fig. 42.

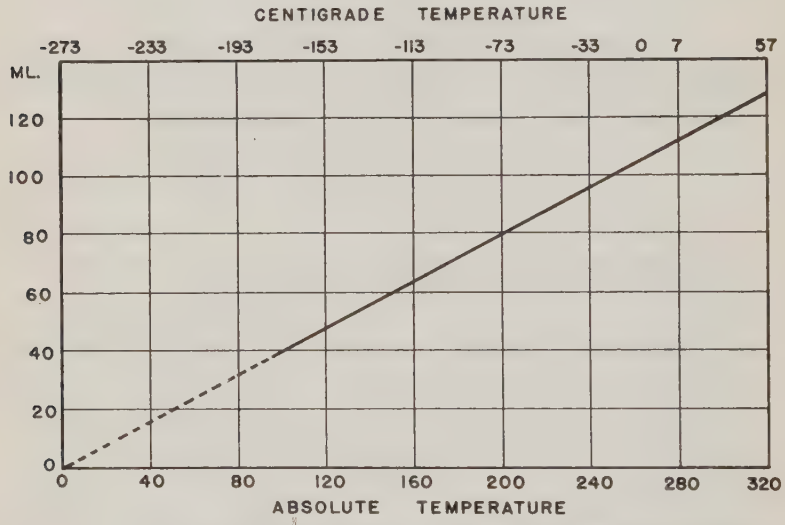


Fig. 42. How the regular decrease in the volume of a gas with temperature leads to the idea of an absolute zero.

Lord Kelvin showed that a temperature scale could be constructed such that the absolute zero was the zero point and the freezing point of water was represented by 273°. This scale of temperature is known as the *Absolute* or *Kelvin* scale and temperatures based on this scale are designated by A, as 25°A. In mathematics, temperature in general may be represented by t but the capital letter T is always used to denote absolute temperatures.

If a volume of gas is trapped in a bulb by means of a small drop of mercury in a graduated tube which is open to the atmosphere, the gas will be subjected to constant pressure. If the bulb is now exposed to different temperatures the drop of mercury will move in the tube as the volume changes and the change in volume may be read from the scale. This is shown in the diagram in Fig. 43. If the original volume of the gas is 120 ml. and the initial temperature is 27°C., the changes in volume and temperature as well as the ratio V/T are given in Table 8.

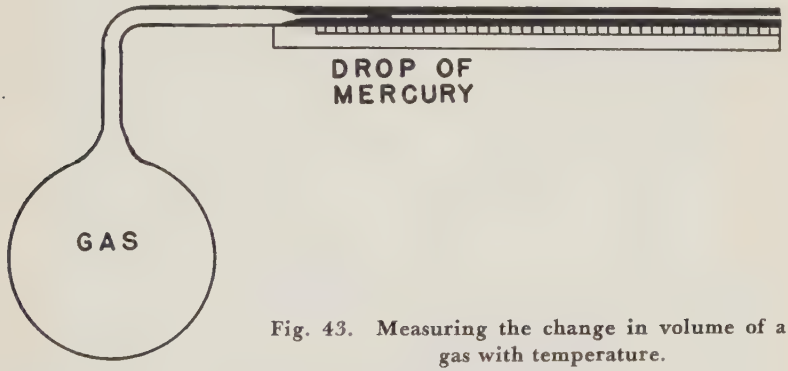


Fig. 43. Measuring the change in volume of a gas with temperature.

TABLE 8—VARIATION OF THE VOLUME OF A GAS WITH TEMPERATURE

Volume (V) *Millilitres*	*Temperature (t)* *Centigrade*	*Temperature (T)* *Absolute*	*Ratio* *V/T*
120	27	300	0.4
116	17	290	0.4
109	0	273	0.4
104	−13	260	0.4
100	−23	250	0.4
80	−73	200	0.4
40	−173	100	0.4
12	−243	30	0.4
4	−263	10	0.4
0	−273	0	—

The last column of Table 8 shows a surprisingly simple relationship between the volume and the absolute temperature. This relationship is known as Charles' Law. *The volume of a given mass of gas under constant pressure varies directly as the absolute temperature.* It will be noted that the temperature *must* be expressed on the Absolute scale so that we have

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

where V_1 and T_1 represent the initial volume and temperature while V_2 and T_2 represent the final volume and temperature.

5. The application of Charles' Law. Let us apply this law to a definite problem. What will be the volume at 12°C. of a mass of gas which has a volume of 150 ml. at 25°C.?

Step I. Distinguish carefully between the initial and final states.

	Volume (V)	*Temperature* (T)
Initial	150 ml. (V_1)	$25 + 273 = 298°$ A (T_1)
Final	? (V_2)	$12 + 273 = 285°$ A (T_2)

Remember to convert from Centigrade to the Absolute scale.

Step II. Make the correction by Charles' Law. As in the case of Boyle's Law there are two methods by which the corrections may be made.

Method A: This is the method of common sense. Think! An increase in temperature expands a gas, a decrease in temperature contracts the gas. The final temperature is lower so that the volume of the gas will be decreased in proportion to the change in the Absolute temperature. The volume will be decreased by multiplying it by a fraction whose numerator is less than its denominator. The new volume will be thus obtained by the following calculation:

$$150 \times \tfrac{285}{298} = 143.5 \text{ ml.}$$

Method B: This is a method of substitution in formulas for those who do not think out problems for themselves. You should not substitute in a formula when it is quicker and more reliable to think out the nature of the change. The formula used is one of the pairs of equal ratios shown in the preceding paragraph: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ or $V_2 = \frac{V_1 \times T_2}{T_1}$.

Substituting the values given in the problem we have

$$V_2 = \frac{150 \times 285}{298} = 143.5 \text{ ml.}$$

This method requires great care in distinguishing quantities and should always be checked by reasoning as in Method A.

In problems concerning the temperature of gases you will have many where you must convert temperature readings from one scale to another. You are advised to review the methods given in Chap. 3, for changing temperatures from Centigrade to Fahrenheit or vice versa, and you are reminded that Charles' Law will only apply in the case of Absolute temperatures.

6. The Ideal Gas Law. The changes in volume due to changes in both temperature and pressure may be calculated easily if one considers one effect at a time. Suppose that a given mass of gas is affected by an increase in pressure and a decrease in temperature. Let us allow the temperature to remain constant and examine the effect of the pressure change. We find that the volume will be reduced as a result of the increase in the pressure. Having examined the effect of the pressure change let us keep the pressure constant and examine the effect of the temperature. The lowering of the temperature will cause a further reduction of the volume. One effect operates upon the result of the other and it does not matter which is considered first. If both temperature and pressure are changing at the same time, each effect is multiplied by the other at every instant, and the net result is the same as if one effect had been completed and the other then allowed to take place. If we label the initial states as V_1, P_1, T_1, and the final states as V_2, P_2, T_2, we can write;

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

This is the Ideal Gas Law and it represents Boyle's and Charles' Laws combined.

7. Law of Pressures. If the volume of a given mass of gas is kept constant while the temperature is increased it is easily recognized that the pressure of the gas will become

greater due to the tendency of the gas to expand. The increase with each increment of temperature will be the same as was found for the volume so Charles' Law is often said to apply to pressures as well as to volumes. If it is stated so as to apply to pressures it is known as the *Law of Pressures*. *The pressure of a given mass of gas at constant volume varies directly with the Absolute temperature.* The Absolute temperature is therefore used for pressure corrections.

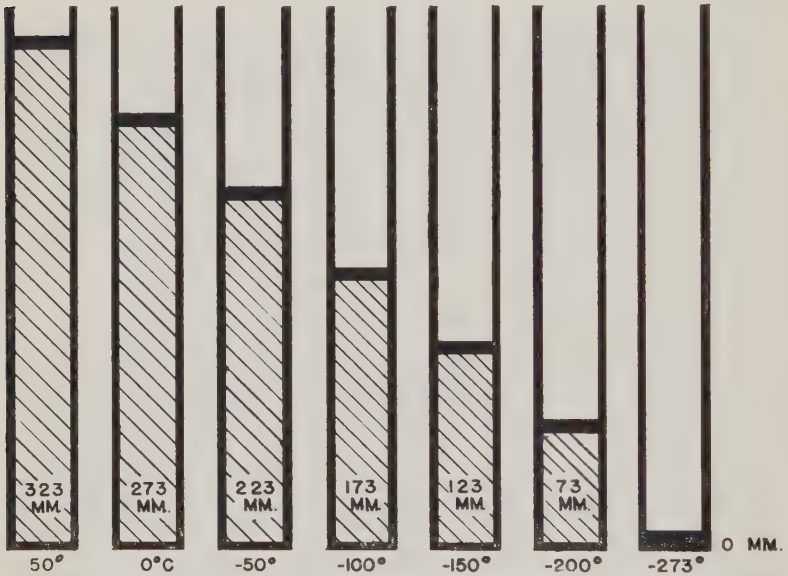


Fig. 44. How a decrease in temperature decreases the pressure of a gas when the volume is constant.

8. Applications of the Ideal Gas Law. By means of the Ideal Gas Law changes in any one of the three variables may be calculated if the changes in the other two are known. To do this two methods are available as before.

Let us consider the following problem. A certain mass of gas has a volume of 356 ml. at a pressure of 714 mm. of mercury and a temperature of 25°C. What will be its volume at a pressure of 560 mm. of mercury at a temperature of 3°C.?

Step I. Arrange to distinguish the states and the variables.

	Volume	*Pressure*	*Temperature*
Initial	365 ml. (V_1)	714 mm. (P_1)	25°C. or 298°A (T_1)
Final	? (V_2)	560 mm. (P_2)	3°C. or 276°A (T_2)

Step II. Make the calculations by the gas law.

Method A: By simply reasoning out the effect of each change.

(*i*) The effect of the pressure change is to increase the volume by removing a part of the applied pressure. The new volume after the pressure change alone will be

$$356 \times \tfrac{714}{560} \text{ ml.}$$

(*ii*) The effect of the temperature change is to decrease this new volume by the ratio of the Absolute temperatures, so that the final volume will be

$$356 \times \tfrac{714}{560} \times \tfrac{276}{298} \text{ ml. or } 420 \text{ ml.}$$

Method B: By substitution in the formula.

$$\text{Solving } \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ for } V_2, \text{ we get, } V_2 = \frac{P_1V_1T_2}{P_2T_1}$$

By substituting the values given in the problem we have

$$V_2 = \frac{356 \times 714 \times 276}{560 \times 298} = 420 \text{ ml.}$$

This can be verified by the simple reasoning given above.

9. The density of gases. The density of a gas, like the density of a solid or a liquid, is the mass per unit volume. Since the weight of a millilitre of a gas is very small, it is more convenient to adopt the weight of one litre instead and this is the so-called *normal density*, or just *density*. In stating the volume of a gas the temperature and pressure must be specified, and a *standard temperature* and *pressure* have been selected. We speak of the standard temperature and pressure S.T.P., (sometimes the word "normal" instead of "standard" is used and the expression is written as N.T.P.) as the freezing point of pure water, 0°C. and the average air pressure at sea level 760 mm. of mercury.

If the weight of a volume of gas at any temperature and pressure is known its density may be calculated by the application of the gas laws. For example: If 500 ml. of a gas

at 27°C. and 700 mm. of mercury weigh 0.70 g., what is its density?

Step I. The first thing to do is to find the volume of the gas under standard conditions.

$$500 \times \frac{273}{298} \times \frac{700}{760} = 421.9 \text{ ml.}$$

Step II. Since the weight cannot be altered, the weight of 500 ml. of the gas under the initial conditions must be the weight of 421.9 ml. under standard conditions. So, if 421.9 ml. weigh 0.70 g., one litre will weigh

$$0.70 \times \frac{1000}{421.9} = 1.66 \text{ grams.}$$

The density of gases is also given in relative terms by comparing the weight of any volume of the gas to the weight of an equal volume of another gas, under the same temperature and pressure. The gas chosen as a standard is usually hydrogen, since it is the lightest gas; but air is sometimes used in special cases and in older tabulations.

The normal densities of some of the common gases and vapours will be important in later discussions and are given in Table 9.

TABLE 9—MODERN EXACT VALUES FOR THE WEIGHT IN GRAMS OF ONE LITRE OF VARIOUS GASES AT STANDARD TEMPERATURE AND PRESSURE

Gas	*Weight of 1 litre*	*Gas*	*Weight of 1 litre*
Air	1.2927	Methane	0.7168
Ammonia	0.7708	Nitric oxide	1.3402
Carbon dioxide	1.9768	Nitrogen	1.2506
Carbon monoxide	1.2504	Nitrous oxide	1.9777
Hydrogen	0.0899	Oxygen	1.4290
Hydrogen chloride	1.6392	Sulphur dioxide	2.9267

Each of the gas laws deals with the change in the *volume* of a *fixed mass of gas*. You realize that *the volume, at a fixed temperature and pressure, varies directly as the mass or weight of the gas*. Twice as great a weight of gas will occupy twice as large a volume when both are measured at the same temperature

and pressure. It follows that the pressure exerted in a *fixed* volume at a given temperature will depend on the weight or amount of gas present. The method used to find the density of the gas at S.T.P. can be used to calculate the weight occupying a given volume under any specified conditions of temperature and pressure if the density or the weight of a known volume under given conditions is known.

Let us use this principle, that increased mass means increased volume or pressure at the same temperature to solve some problems.

Example 1. If 1 gram of oxygen occupies 0.7 litres at a certain temperature and pressure, what is the volume occupied by 32 grams of oxygen under the same conditions?

The answer is obvious, $32 \times 0.7 = 22.4$ litres.

Example 2. When 2 grams of carbon dioxide are confined in a 200 ml. flask at a certain temperature the pressure is 5 atmospheres. What weight of carbon dioxide will the flask contain at this temperature at atmospheric pressure?

We realize the quantity is proportional to the pressure so it is $\frac{1}{5} \times 2$g. $= 0.4$ g.

Example 3. If 3 grams of a gas occupy 7 litres at 40°C., what volume will 5 grams occupy at 0°C., if the pressure is constant?

Step I. Find the volume occupied by the 3 grams of gas at 0°C. By Charles' Law it is $\frac{273}{313} \times 7 = 6.1$ litres.

Step II. If 3 grams occupy 6.1 litres at 0°C., therefore 5 grams will occupy $\frac{5}{3} \times 6.1$ litres $= 10.2$ l. at 0°C.

Example 4. If 10 lb. of a gas occupy 140 ft.^{3} at 27°C. and 700 mm. pressure what volume will 1 ton occupy at 62°C. and 800 mm. pressure.

Step I. Find the volume occupied by the fixed mass (10 lb.) under the new conditions.

$$140 \times \frac{335}{300} \times \frac{700}{800} = 137 \text{ ft.}^3$$

Step II. Find the volume occupied by 1 ton (2000 lb.).

$$\frac{2000}{10} \times 137 = 27{,}400 \text{ ft.}^3$$

Example 5. If 12 grams of gas occupy 35 l. at 40°C. and 500 mm. pressure, find the weight of it required to fill a balloon which holds 10,000 litres at 22°C. and 760 mm. pressure.

If you remember that the proportionately greater weight can be found only when the two volumes are measured at the *same temperature and pressure* you will say to yourself: "Now if I knew how many litres measured at 40°C. and 500 mm. pressure it would take to make 10,000 litres at 22°C.

and 760 mm. pressure, I could find the weight by simple proportion. This I can find by first correcting the volume required to fill the balloon to the temperature and pressure at which I know the weight of the gas".

Step I. Find the volume of gas at 40°C. and 500 mm. required to fill the balloon.

$$10{,}000 \times \tfrac{313}{295} \times \tfrac{760}{500} = 16{,}130 \text{ litres.}$$

Step II. Now the weight required is easily found.

$$\tfrac{16130}{35} \times 12 \text{ g.} = 5{,}570 \text{ g.}$$

Example 6. If the pressure in a gas cylinder is 2000 lb. per square inch when it contains 12 lb. of gas at 27°C., what is the pressure when half the gas has been used and the temperature is 12°C.?

Step I. Find the new pressure at 27°C.

$$2000 \times \tfrac{6}{12} = 1000 \text{ lb. per square inch.}$$

Step II. Use the Law of Pressures.

$$1000 \times \tfrac{285}{300} = 950 \text{ lb. per square inch.}$$

10. Dalton's Law of Partial Pressures. Experimenting with gases was in great vogue at the end of the eighteenth century and among the experimenters was John Dalton. He showed that *the total pressure of a mixture of gases is the sum of the partial pressures which each gas would exert if it occupied the whole space alone.* The pressure relationship is known as Dalton's Law of Partial Pressures.

This law is of great practical use in correcting the volumes of gases measured over liquids and particularly over water. When a liquid is admitted to an empty space it evaporates until a definite pressure of its vapour exists over the liquid surface. The amount of this vapour pressure depends upon the temperature and increases quite rapidly if the temperature is raised and decreases if the temperature is lowered. Most substances have almost no vapour pressure in the liquid or solid form at the temperature of liquid air (-195°C. to -185°C.), so they may be freed from air by pumping at this temperature. As they warm up the vapour pressure may be recorded at different temperatures. A vapour pressure or vapour tension table for water is given in Chap. 15, sec. 5.

The mechanical equipment for the precise measurement and manipulation of gases is rather complicated but it can be shown that if we have an evacuated space connected to a manometer as shown diagramatically in 1 of Fig. 45, and we admit 100 ml. measured at S.T.P. of a certain gas to the space it will produce a pressure as shown on the manometer in 2 of Fig. 45. If we now evacuate the space again and add 100 ml. measured at S.T.P. of another gas it will produce a similar pressure as shown in 3. If now 100 ml. measured at S.T.P. of the first gas be added to the space which already contains 100 ml. of the second gas the pressure will be double that of either gas in the space alone. The mixture will behave just like 200 ml. of either gas measured S.T.P. would behave in the same space (see 4 of Fig. 45).

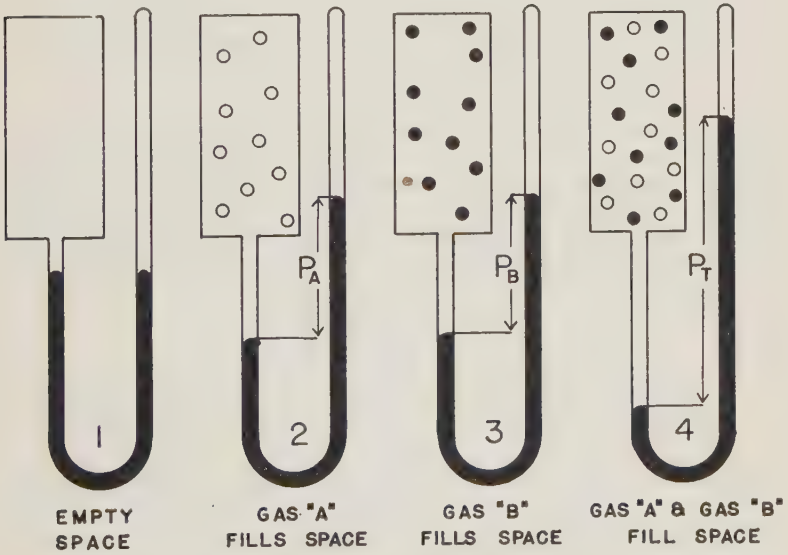


Fig. 45. Dalton's Law of Partial Pressures.

The only instance when this would not be true is when the two gases react with one another. The extent of reaction between gases is actually measured by their failure to obey

this law. When gases are collected over liquids which have appreciable vapour pressures the mixture of gas and vapour fills the space and the two produce the pressure. If the pressure on a gas collected over water is given, it represents the *total* pressure exerted by both the gas and the water vapour at that temperature. By subtracting the vapour pressure due to the water, the net pressure exerted by the dry gas in the same volume is obtained.

Total pressure = pressure of gas + pressure of water vapour

The application of this law may be shown in the following example, which is similar to those considered previously but in which the pressure given is that of the gas mixture collected over water. Find the volume of a mass of dry oxygen at S.T.P. which has a volume of 350 ml. measured over water at 18°C. and 749 mm. pressure. The vapour pressure of water at 18°C. is 15.48 mm.

Step I. Find the pressure of the dry gas in the initial state. The pressure of 749 mm. is that exerted by the gas and the water vapour. Since we know that the water vapour pressure at 18°C. is 15.48 mm., we must subtract that amount from the total given pressure to obtain the pressure due to the dry gas. Subtracting 15.48 from 749 gives 733.52, so the pressure of the dry gas in the initial state is 733.52 mm.

Step II. Distinguish between the initial and final states.

	Volume	*Pressure of dry gas*	*Temperature*
Initial	350 ml.	733.53 mm.	18°C. (391° A)
Final	? ml.	760 mm.	0°C. (273° A)

Step III. Apply the Ideal Gas Law. Note that we have eliminated the effect of the water and are considering the dry oxygen alone. Using the method of reasoning we get:

$$350 \times \frac{733.52}{760.00} \times \frac{273}{291} = 317 \text{ ml.}$$

11. Henry's Law. Another factor involved in the collection of gases over water is their solubility in the water. The three factors which determine the solubility are:

(1) the chemical nature of the gas and the liquid;

(2) the temperature, since an increase in temperature decreases the solubility of a gas so that its solubility approaches zero at the boiling point of the liquid;

(3) the effect of the pressure. The effect of the pressure is known as Henry's Law, which states that the *weight of a gas dissolved by a given volume of a liquid at a constant temperature is proportional to the pressure of the gas.*

Some gases, like hydrogen, nitrogen and oxygen, are only slightly soluble in water; others, like carbon dioxide and chlorine, are moderately soluble; and some, like ammonia and hydrogen chloride, are extremely soluble. The gases which are very soluble in water do not obey Henry's Law closely and even carbon dioxide shows large deviations at more than a few atmospheres' pressure.

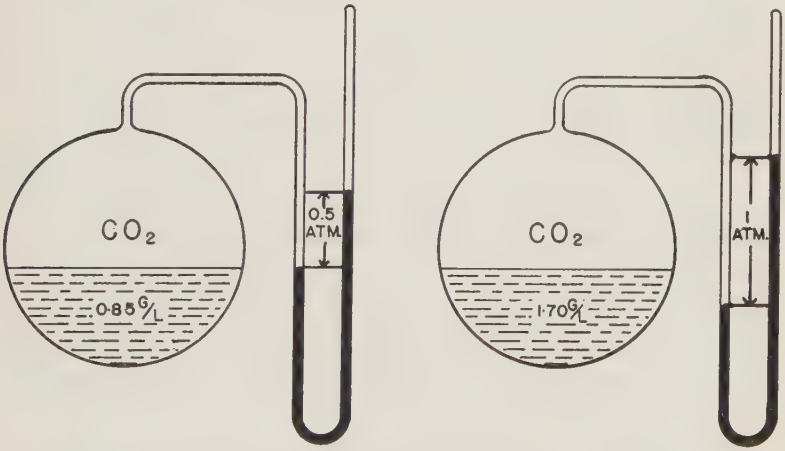


Fig. 46. Henry's Law. The amount of the gas dissolved by the liquid is proportional to the pressure of the gas above the solution.

If 100 millilitres of water dissolves 1.70 grams of carbon dioxide at 1 atmosphere pressure we would predict from Henry's Law that it would dissolve 1.70 × 3, or 5.1 grams of the gas at a pressure of 3 atmospheres. The familiar bottle of carbonated beverage is a good example of Henry's Law. When the cap is removed the excess gas escaping when the pressure is decreased causes effervescence.

Question Summary

1. Why do untrained people find it hard to appreciate the gas laws?

2. (*a*) How does a change in pressure affect the volume of any gas at constant temperature?

(*b*) How must the pressure vary if the volume of a given mass of gas doubles?

3. (*a*) Plot the pressure values in Table 7 as ordinates against the volumes as abscissae and so make a graph to show inverse proportion.

(*b*) What causes the air to rush out of an automobile tire when a blow-out occurs?

4. (*a*) Why is Charles' Law so named when Dalton and Gay-Lussac enunciated it?

(*b*) State Charles' Law in terms of expansion on the Centigrade scale.

(*c*) Give the argument for an absolute zero of temperature on a gas thermometer.

(*d*) How are Centigrade temperatures converted to Absolute temperatures?

5. (*a*) State how an increase in temperature affects the volume of a confined mass of gas.

(*b*) State how you derive the formula $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ from Charles' Law.

(*c*) If the Absolute temperature of a mass of gas is decreased to one-half of its original value, how is the volume of the gas affected at constant pressure?

6. (*a*) Explain how there might be no change in volume due to a change in both temperature and pressure.

(*b*) Can you calculate the change in volume of a gas due to a 30°C. increase in temperature without being given the initial temperature? Why?

7. (*a*) State the Law of Pressures.

(*b*) Give an argument for an absolute zero of temperature by means of the Law of Pressures.

8. Explain the use of the Ideal Gas Law.

9. Why is it necessary to give the temperature and the pressure when you are stating the weight of a gas per unit volume?

10. (*a*) If air is one-fifth oxygen and four-fifths nitrogen by volume, and its total pressure will hold up a column of mercury 760 mm. in height, how high would the oxygen alone raise the mercury column? How high would the nitrogen alone raise it?

(*b*) How does the vapour pressure of most liquids change as the temperature is lowered?

(*c*) Why do we always speak of the pressure of the *dry* gas when we describe its condition of pressure?

11. Why does a bottle of soda water effervesce when you remove the cap?

Problems

1. What is meant by "standard pressure"? What is the standard pressure in (*a*) mm. of mercury; (*b*) cm. of mercury; (*c*) pounds per square inch; (*d*) feet of water; (*e*) tons per square foot?

2. State the effect of the following changes on 1000 ml. of a gas at constant temperature:

(*a*) Doubling the pressure;

(*b*) Reducing the pressure to one-half; to one-third; and to one-quarter of its initial value.

3. Reduce the following gas volumes to standard pressures: 800 ml. at 700 mm. of mercury; 50 ml. at 65 cm. of mercury; 90 cu. ft. at 20 pounds per square inch; 330 cu. ft. at 10 pounds per square inch.

4. Find the pressure in mm. of mercury at which the following volumes measured under standard pressure fill a one-litre flask: 1000 ml., 800 ml., 1250 ml., 2500 ml.

5. An ammonia generator has a volume of 45 gallons and the gases are under 400 atmospheres pressure. How much space would they occupy if released at atmospheric pressure?

6. Convert the following Fahrenheit temperatures to Absolute: 212°, 32°, 122°, 77°, −157°, −458°.

7. A given mass of helium has a volume of 546 ml. at 0°C. What is its volume at 1°C., −5°C., 100°C., −73°C., and −250°C.?

8. A certain weight of a gas has a volume of 300 ml. at 27°C. What is its volume at −73°C.?

9. A student collected 100 ml. of oxygen when the temperature was 25°C. The room cooled down to 15°C. overnight. What was the volume change on cooling?

10. Suppose you had a quantity of gas which had a volume of 130 ml. at −13°C., how would you find its volume at 27°C.? What kind of result would you get if you happened to forget to change the Centigrade temperatures to Absolute temperatures?

11. Can you calculate the change in volume of a gas due to doubling its Centigrade temperature without knowing the Centigrade temperature? Explain.

12. If a mass of helium has a volume of 600 ml. at 27°C., at what temperature would it have a volume of 500 ml., 1000 ml., 200 ml., 448 ml., 20 ml.?

13. Correct the following gas volumes to standard temperature: 100 ml. at 100°C., 76 ml. at 20°C., 150 ml. at −40°F., 2760 ml. at 68°F., 28,660 ml. at 33°C.

14. Reduce each of the following volumes to S.T.P.:
(*a*) 1500 ml. measured at 27°C. and 570 mm.
(*b*) 95 ml. measured at −33°C. and 720 mm.
(*c*) 30.4 ml. measured at 31°C. and 606 mm.

15. Find the volume of 1200 ml. of gas at S.T.P. when the conditions are changed to:
(*a*) 91°C. and 600 mm.
(*b*) −23°C. and 1000 mm.
(*c*) 182°C. and 950 mm.

16. Find the pressure which 1 litre of gas at 1 atmosphere pressure would exert if the volume was held constant when it is heated from −23°C. to 102°C.

17. If an automobile tire is inflated to a pressure of 30 pounds per square inch at 32°F. and it heats up to 122°F. on driving the car, what does the pressure become?

18. A mass of gas has a volume of 500 ml. at 7°C. and 760 mm. If the pressure is changed to 570 mm., what must the temperature become to keep the volume constant?

19. Calculate the densities of the following gases:
(*a*) 250 ml. at S.T.P. weighs 0.3232 g.
(*b*) 50 ml. at S.T.P. weighs 0.1463 g.
(*c*) 300 ml. at S.T.P. weighs 0.2312 g.

20. Find the density of the following gases, if:
(*a*) 238 ml. at 27°C. and 880 mm. weighs 0.1792 g.;
(*b*) 25 ml. at −33°C. and 660 mm. weighs 0.04944 g.;
(*c*) 418 ml. at −63°C. and 700 mm. weighs 1.4633 g.

21. (*a*) What is the weight of 22.4 litres of air? Of .15 litres of carbon dioxide? (See Table 9).

(*b*) How many litres will 100 g. of the following gases occupy at 27°C. and 700 mm. pressure? (*i*) hydrogen; (*ii*) methane; (*iii*) sulphur dioxide.

(*c*) If 20 g. of a gas occupy 50 litres at 42°C., what volume will be occupied by 250 ml. at 17°C. if the pressure is constant?

22. (*a*) If 2.4 g. of a gas are contained in 7 litres at 40°C. and 550 mm. pressure, what volume will be required for 30 g. at S.T.P.?

(*b*) In preparing oxygen a student collected 420 ml. of oxygen with a loss in weight of 0.500 g. If the temperature of the oxygen was 22°C.

and its pressure was 690 mm., what weight did he find for 22.4 litres of oxygen at S.T.P.?

(*c*) If 8 g. of methane exerts a pressure of 1.5 atmospheres in a container at −80°C., what pressure will 12 g. exert in the same size of container at 152°C.?

23. What is the partial pressure of each gas in a mixture of gases at atmospheric pressure which is 25% nitrogen, 40% carbon dioxide, and the remainder carbon monoxide?

24. If a certain mass of a gas which is insoluble in water has a volume of 300 ml. at S.T.P., what volume will it have over water at 20°C. and 717.53 mm.?

25. A student collected 464 ml. of oxygen over water at 26°C. when the barometric pressure was 745.21 mm. The loss in weight of the potassium chlorate used to prepare it was 0.285 g. Find the density of the dry oxygen at S.T.P.

26. The solubility of oxygen is 43.4 mg. per 1000 g. of water at 20°C. when the pressure of the oxygen is 760 mm. If the air is one-fifth oxygen, how much oxygen is required to saturate 1000 g. of water exposed to the atmosphere?

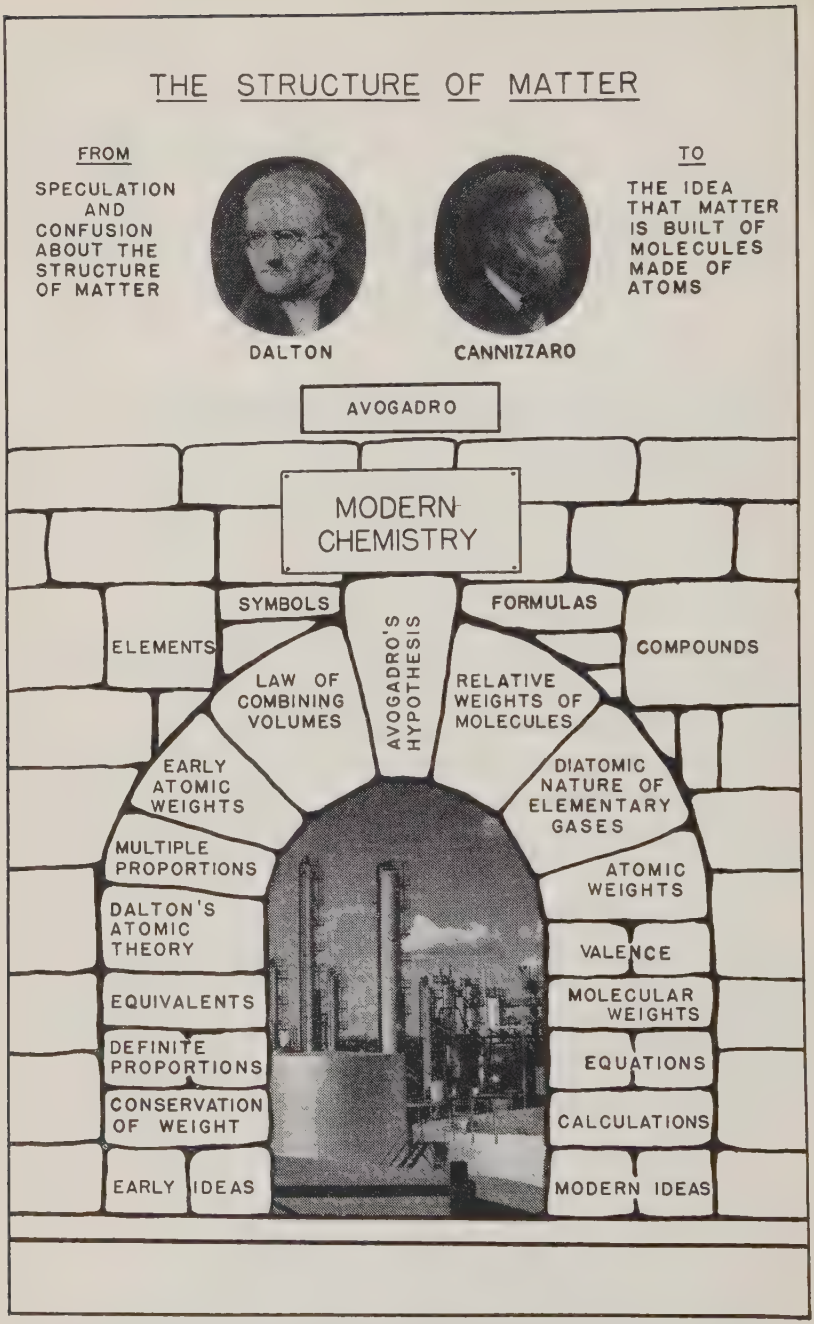
27. If 1.70 g. of carbon dioxide dissolves in 1000 g. of water at 20°C. when the pressure is 760 mm., how much will dissolve in 200 ml. of water at 20° if the pressure is 5 atmospheres?

Topic Two

THE RIDDLE OF MATTER'S STRUCTURE

You have seen how men solved the mystery of fire and determined the nature of water. By applying pure reason and exact measurement to the reactions between gases, liquids and solids they were able to determine not only the nature of the elements in them but finally the number of ultimate particles of each element. This stupendous advance in knowledge laid the foundation for our modern scientific achievements.

A system of shorthand for indicating the structure of pure substances was evolved and methods for the exact prediction of the results of reactions devised. To show you the far-reaching consequences of these discoveries we will also give you a quick review of what modern man has learned about the internal structure of what men of the nineteenth century believed to be ultimate particles of matter.


THE STRUCTURE OF MATTER
FROM
SPECULATION AND CONFUSION ABOUT THE STRUCTURE OF MATTER
DALTON
CANNIZZARO
TO
THE IDEA THAT MATTER IS BUILT OF MOLECULES MADE OF ATOMS
AVOGADRO
MODERN CHEMISTRY
SYMBOLS
FORMULAS
ELEMENTS
COMPOUNDS
LAW OF COMBINING VOLUMES
AVOGADRO'S HYPOTHESIS
RELATIVE WEIGHTS OF MOLECULES
EARLY ATOMIC WEIGHTS
DIATOMIC NATURE OF ELEMENTARY GASES
MULTIPLE PROPORTIONS
ATOMIC WEIGHTS
DALTON'S ATOMIC THEORY
VALENCE
EQUIVALENTS
MOLECULAR WEIGHTS
DEFINITE PROPORTIONS
EQUATIONS
CONSERVATION OF WEIGHT
CALCULATIONS
EARLY IDEAS
MODERN IDEAS

Chapter 8

Early Atomic Ideas

1. Introduction. The last topic described the beginnings of chemistry: how men learned to distinguish elements, compounds, mixtures, gases, liquids, and solids; how they came to understand the nature of fire and a host of other chemical changes; and finally how they found laws about the general behaviour of gases. Now we will see that by applying pure reason to the data they had collected they were able to draw far-reaching conclusions about the structure of matter itself. These conclusions made possible the vast developments in chemistry during the last hundred years.

2. Law of Conservation of Weight. The basic law about chemical changes was realized before the birth of Christ but Lavoisier gave it a quantitative statement based on precise experimental evidence. He said:

"Nothing can be created, and in every process *there is just as much substance present before and after the process has taken place.*"

This is the Law of Conservation of Mass or Weight or the Law of the Indestructibility or Durability of Matter.

There are many apparent examples of the destruction of matter in the burning of sulphur, phosphorus, and carbonaceous material such as wood, wax, oil, etc. Most of these apparent examples are due to the escape of gases or vapours. Since neither the existence of gases nor the technique of capturing and weighing them was known by many before the eighteenth century, it is easy to understand why this principle was not accepted before Lavoisier's time. The method of

proving it in one of these cases is rather simple. A small candle is allowed to burn in a cylinder whose top part is filled with sodium hydroxide supported on quicklime or asbestos. The whole is carefully balanced and the candle is lighted. As the carbon dioxide and water vapour are caught in the quicklime and soda the weight soon increases because of the addition of oxygen to the combustible material. This is shown in Fig. 47.

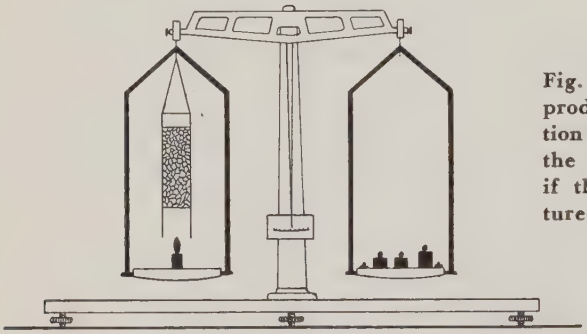


Fig. 47. The gaseous products of combustion weigh more than the original material if they are all captured and weighed.

The most famous experiments were those of Landolt which required some fifteen years of patient expert work for their perfection. They were simple in principle. In the separate legs of hermetically sealed U-tubes which held nearly a litre (1000 g.), he placed the two reactants. The ones chosen reacted completely without the production of much heat or volatile products. The filled tubes were carefully weighed to 0.0001 g. or one part in ten million. They were inverted until the reaction was complete and cooled to the original temperature before being reweighed. If all errors due to changes in surface moisture or volume of the tubes were eliminated it was found that the change in weight was less than one part in ten million. For these reactions we know the Law of Conservation of Mass held within the limits of the experimental error. The experiments were completed in 1908 (see Fig. 48).

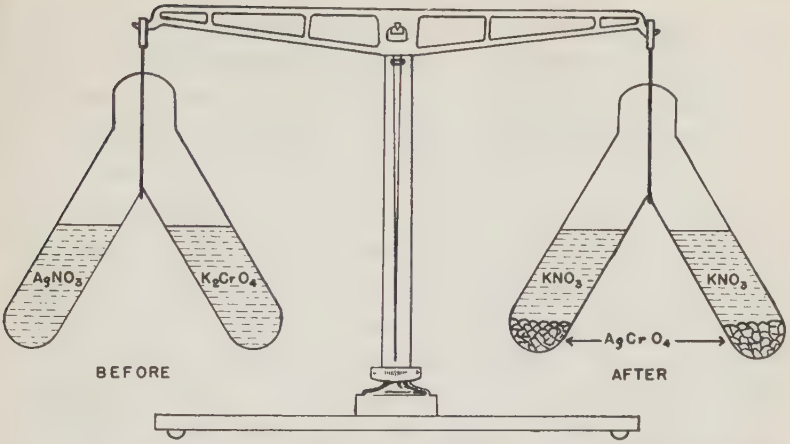


Fig. 48. Landolt's experiment. The products weigh the same as the reactants.

3. Law of Definite Proportions or Constant Composition. This law simply states that *the composition of a pure substance is always the same.* To view this from the standpoint of the weights of the reactants which go into the formation of the new compound we may state the law in another way:

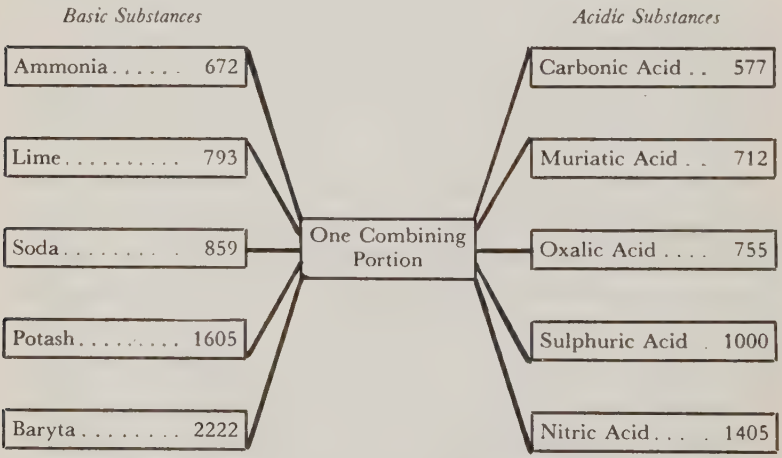
"*The proportions by weight of the substances that react to form a pure compound are always the same.*"

This is illustrated in the work on the synthesis of water (see Chapter 6). The proportion of hydrogen to oxygen by weight is always 1.008 g. of hydrogen to 8.000 g. of oxygen. In the formation of a sulphide of lead from its elements 2.0732 g. of lead will unite with only 0.3206 g. of sulphur. Any excess of sulphur will burn away. The composition of water or lead sulphide is always the same regardless of the manner of preparation, when they have been freed from all impurities.

It is possible for the same two elements to form more than one pure compound by combining in more than one definite ratio. In each pure compound the proportions by weight of

the constituents are constant. Thus sulphur dioxide is always 50 per cent sulphur and 50 per cent oxygen while sulphur trioxide is always 40 per cent sulphur and 60 per cent oxygen.

4. Law of Equivalents or Unit Reacting Weights. In 1766 Cavendish found that the weight of lime required to neutralize 100 g. of sulphuric acid was not the same as the weight of potash required to neutralize the same weight of the acid, but he recognized that these two different weights of lime and potash are *equal to one another in neutralizing power.* He called them *equivalent weights* or *equivalents.* We could also call them combining proportions or reacting weights. In 1788 he pointed out that the weights of nitric acid or of sulphuric acid which would neutralize a given weight of lime were the same ones which would neutralize a given weight of potash different from that of the lime. He therefore proposed that these were equivalent weights, that is, equivalent in neutralizing power.


Basic Substances
Acidic Substances
Ammonia 672
Lime 793
Soda 859
Potash 1605
Baryta 2222
One Combining Portion
Carbonic Acid . . 577
Muriatic Acid . . 712
Oxalic Acid 755
Sulphuric Acid . 1000
Nitric Acid 1405

The generalization of Cavendish's idea was made by Richter (1792-1794) and may be called the Law of Unit Reacting Weights, which is another name for these defined

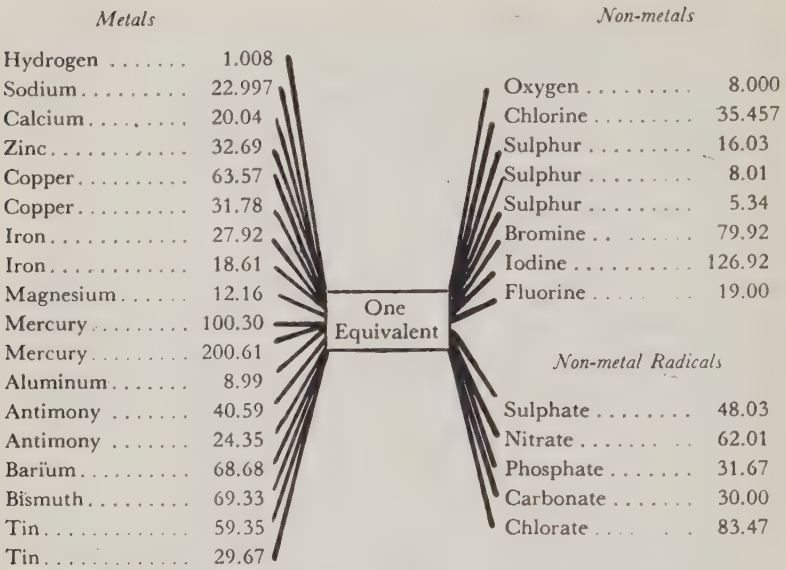
combining proportions which we now call equivalents. The first table of equivalent weights is reproduced above in the form of a telephone exchange where the basis of exchange or neutralization is one kilogram of sulphuric acid, or the quantity which reacts with it or is equal to it.

The translator of Berthollet's *Researches on the Laws of Affinity* renders the explanation as follows:

"The meaning of this table is that if a substance is taken from one of the two columns, say potash from the first, to which corresponds the number 1605, the numbers in the other column indicate the quantity of each acid necessary to neutralize these 1605 parts of potash. There will be required 712 parts of muriatic acid, 577 parts of carbonic acid, etc. If a substance is taken from the second column, the first column is to be used to ascertain how much of an earth or an alkali is required to neutralize it."

Wenzel, as early as 1777, appears to have made analyses of compounds in order to determine the combining proportions or reacting weights of the elements but did not find a basis of comparison upon which a table could be constructed. Shortly after, Richter proposed his law of reacting weights or reciprocal proportions as they were then called, the analytical data was carefully examined and it appears that 1 g. of hydrogen was chosen at that time as a standard for reacting weights or combining proportions. We may construct a modern table of the metals and non-metals similar to that just given for the bases and acids. We now use 1.008 g. of hydrogen as a basis and the *gram equivalent weight is defined as that weight which combines with or displaces 1.008 of hydrogen or its equivalents, 8.000 g. of oxygen or 35.457 g. of chlorine.*

This is only a partial table of the elements but it shows the application of the Law of Equivalents or Unit Reacting Weights, which may be stated in a manner similar to that for acids and bases: *For each element a number may be chosen so that when it combines with another element either that number of grams, or some multiple or sub-multiple of it, is involved.*



It will be observed that the law is more complicated for elements than for acids and bases, because they have the power to combine in more than one proportion to form pure compounds. You will notice that copper has two gram equivalent weights, 63.57 g. and 31.78 g. respectively. These correspond to the two oxides it can form, cuprous oxide which is a brick-red colour, and cupric oxide which is black. These are the same two equivalent weights of copper which may be found in cuprous sulphide and cupric sulphide and similar pairs of copper compounds. The same is true for iron, mercury, antimony, arsenic, bismuth, carbon, chromium, cobalt, nickel and other elements. Some metals have only one equivalent weight. Among these are lithium, sodium, potassium, magnesium, calcium, barium, zinc, cadmium and aluminum. This explains the additional statement that they combine in characteristic weights, or simple multiples or sub-multiples of them. Thus 63.57 g. of copper combine with 8.000 g. of oxygen to form 71.57 g. of cuprous oxide

or 31.78 g. of copper combine with 8.000 g. of oxygen to form 39.78 g. of cupric oxide. The first weight of copper is twice the second weight.

Such a table of equivalents enables us to work out the composition of all the compounds formed by the combination of the metals with the non-metals. A metal is often found combined with more than one non-metal in certain compounds. Some of these combinations, called radicals, are shown in the table. It is much simpler to consider radicals as wholes than to consider the equivalent weights of the separate elements combined in them. For example, calcium sulphite, $CaSO_3$, and calcium sulphate, $CaSO_4$, show sulphur in combination with different weights of oxygen but the same weight of calcium.

The equivalent or unit reacting weight of an element is most easily calculated from the composition of its oxide. Consider the oxides of sulphur mentioned previously. Sulphur dioxide is 50 per cent oxygen and 50 per cent sulphur, or, 50 g. of sulphur reacts with 50 g. of oxygen. By definition, the unit reacting weight or equivalent is the weight which reacts with 8.000 g. of oxygen. This is obviously 8.000 g. of sulphur in this compound.

Sulphur trioxide is 40 per cent sulphur and 60 per cent oxygen and if you wish to use a system for finding the equivalent weight, you may say:

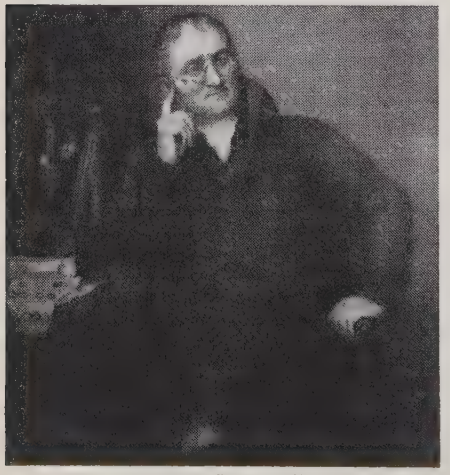
Step I. Change the percentages to weights in 100 g. Thus 40 g. of sulphur combines with 60 g. of oxygen.

Step II. Find the weight of the element which combines with the defined combining weight, 8.000 g. of oxygen. Thus $40 \times \frac{8}{60} = 5.33$ g. is the equivalent weight of sulphur in the trioxide.

Equivalent weights are relative numbers and any units may be used with them instead of grams if the same units are used with all the other substances involved.

The understanding of equivalents is made difficult by the fact that so many names are used for these equivalent quantities. They are called combining weights, combining proportions, reacting weights, reacting proportions, reciprocal proportions, equivalent weights and equivalents, and you can see they are well described by any of these terms. To be precise and quantitative we have had to give an exact definition to those weights based on 1.008 g. of hydrogen and these should be called *equivalent weights*. They may be called unit reacting weights if these words are more meaningful. The terms combining weights, reacting weights, etc. should be used generally to describe fractional or multiple quantities of these equivalents. For example, we may say the reacting weight of sulphur in sulphur dioxide is 50 grams with 50 grams of oxygen, but the equivalent weight is 8.000 g. because it is defined as that weight which unites with 8.000 grams of oxygen.

5. Origins of the atomic theory. The question as to the limit to which we can ultimately subdivide matter is still unanswered but we can now answer a more specific question.



Courtesy Fisher Scientific Co.

Fig. 49. John Dalton (1766-1844), English schoolteacher who stated the atomic theory in a form which permitted its verification. His ideas about the combination of atoms led him to the Law of Multiple Proportions and his experiments on moisture in the air led him to his Law of Partial Pressures.

To what limit can we subdivide matter so that each particle may retain the properties of the pure substance which is being divided? The credit for giving a conclusive answer to this question usually goes to an English schoolmaster, philosopher and research worker, John Dalton. The question he attempted to answer was a very old one—the idea that matter is discontinuous. It can be traced back as far as 1000 B.C. The Greeks debated the question with great vigour from qualitative considerations and by analogy. Some of these arguments are worthy of note.

Everything made of matter suffers continual change. In all this change matter itself appears to be permanent. This can be explained if we assume that the various substances are made of a limited number of different kinds of immeasurably small particles. The change consists only in the rearrangement of these particles into new patterns. The fact that we can smell things at a considerable distance makes us suspect that particles from them travel to our noses through the air. The fact that moving air exerts a pressure although it cannot be seen can be rationalized by considering it to be made of moving particles too small to be seen. The dissolving of substances must be due to the intermingling of infinitely small particles.

One of the most cogent arguments is the fluidity of liquids. It is easily observed that peas, wheat, or sand take the shape of the containing vessel and may be poured from one container to another because the particles roll over one another. It is easy to picture the smoother flow of liquids as being due to the presence of particles, which are too small to see, rolling over one another. These liquids will evaporate and this too can be explained by the loss of the same particles involved in the process of diffusion which enables us to smell things at a distance.

Metals will bend without breaking or they may be pounded into thin sheets and drawn into wires. These properties may be accounted for by saying the particles may be forced to slide over one another. The dissolving of metals in acids is gradual as if layers of particles were being removed.

Some Greek philosophers, among whom was Democritus, favoured the idea that matter is made of particles, and brought the idea to Athens. Aristotle, however, did not use the theory and it was doomed to oblivion until the Renaissance thinkers revived it. Robert Boyle and Isaac Newton used the idea of particles extensively, and, as Dalton was nourished on Newton's philosophy, it is not surprising that he sought an explanation of the laws of chemical combination by means of particles.

6. Dalton's atomic theory. Dalton merely assumed that the characteristic weights or combining proportions of the elements were proportional to the weights of their individual atoms. His assumptions were made so as to explain *quantitatively* the known facts and laws. We may state the essential ideas of his theory.

(1) *The chemical elements consist of very minute indivisible particles of matter, atoms,* which are not changed during chemical reactions. The word *atom* means undivided.

(2) *The atoms are permanent bodies* and cannot be divided, created, or destroyed. This explains the law of conservation of weight or mass.

(3) *All the atoms of the same element are identical* in size, weight and form. The weight of each kind of atom was then to be related to the combining weight.

(4) *Atoms of a compound substance (compound atoms) are produced by the union of simple atoms* in the ratio of small whole numbers. This explained the Law of Equivalent Proportions or Reacting Weights, and the Law of Constant Composition.

7. Law of Multiple Proportions. Now Dalton could derive another law from the combining proportions of the elements. His atomic theory made it very reasonable to expect that "*If two elements combine in more than one proportion, then the two combining weights of the one which combine with the fixed weight of the other element must bear a simple whole number ratio to one another.*" This is known as the Law of Multiple Proportions. There are plenty of examples of this law in the list of equivalents. Consider the two weights of copper which

combine with 8 g. of oxygen. They are 63.57 g. and 31.78 g. Comparing these weights to one another we see they are in the ratio 63.57/31.78 or 2 : 1.

It is usual to illustrate this law by the oxides of sulphur, carbon, or nitrogen (see Fig. 50).

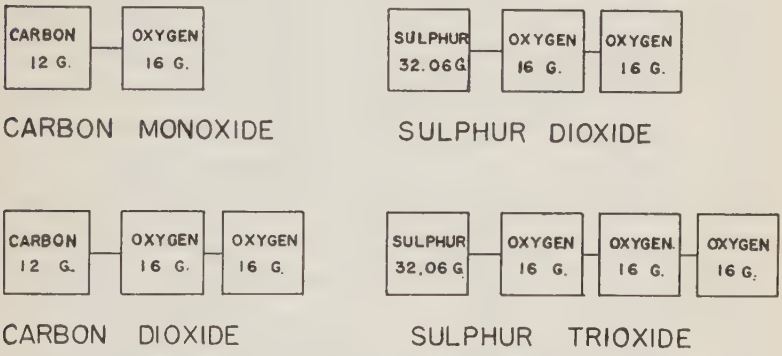


Fig. 50. Dalton's Law of Multiple Proportions.

For a numerical example the percentage compositions of the sulphur oxides quoted earlier will be useful.

1. Sulphur dioxide 50% sulphur, 50% oxygen.
2. Sulphur trioxide 40% sulphur, 60% oxygen.

a. The percentages are easily converted to grams uniting to give 100 grams of the compound.

1. In sulphur dioxide 50 g. of sulphur: 50 g. of oxygen.
2. In sulphur trioxide 40 g. of sulphur: 60 g. of oxygen.

b. Let us first calculate the weights of sulphur combining with a fixed weight of oxygen, say 8 g.

1. Weight of sulphur combined with 8 g. of oxygen in sulphur dioxide $= \frac{8}{50} \times 50 = 8$ g.
2. Weight of sulphur combined with 8 g. of oxygen in sulphur trioxide $= \frac{8}{60} \times 40 = 5.33$ g.

c. Comparing these weights of sulphur with one another we find them as 8 to 5.33 or as 3 : 2.

Alternatively we might calculate the weights of oxygen combining with a fixed weight of sulphur, say 50 g.

a. In sulphur dioxide, 50 g. of oxygen combine with 50 g. of sulphur. In sulphur trioxide, $\frac{60}{40} \times 60$ g. or 75 g. of oxygen combine with 50 g. of sulphur.

b. The weights of oxygen which combine with 50 g. of sulphur are to one another in the ratio of 3 : 2.

According to Dalton's theory the explanation was simple. In one case two atoms of oxygen combine with one atom of sulphur and in the other case three atoms of oxygen combine with one atom of sulphur.

8. The relative weights of the atoms. The absolute weights of the atoms when compared with one another are the relative weights of the atoms. Now the weights which combine with one another are the equivalent weights and it would be very simple if we could declare these to be the atomic weights. This would be true if all elements united in the ratio of one atom to one atom. Dalton knew this was not true in all cases but he could see no other basis for choosing the atomic weight from among the equivalent weights and their possible multiples. He thus made another assumption in addition to the four above.

(5) The commonest compounds are formed when the atoms combine in the simplest ratio.

This means that he assumed that water, being the commonest compound of hydrogen and oxygen, was formed from one atom of hydrogen and one atom of oxygen. Since the combining weights of hydrogen and oxygen in water are 1.008 g. of hydrogen to 8.000 g. of oxygen he assumed these numbers to represent the relative weights of the atoms.

The actual weights of the individual atoms were not known in Dalton's time, but this method required 1.008 g. of hydrogen to contain the same number of atoms as the 8.000 g. of oxygen if the composition was assumed to be one atom of each element per compound atom of water. This fifth assumption could not lead to satisfactory values for the relative weights of the atoms. The problem was thus one of determining how many atoms of each element were contained in a compound atom, or of finding some method for determining the atomic weights which would be *independent* of

combining proportions. Such a method was soon available for the gaseous elements.

Question Summary

1. State briefly what you understand by the term *chemical change.*

2. Why is the Law of Conservation of Weight called the Law of the Indestructibility of Matter?

3. Why do we say that the Law of Definite Proportions is only a statement that compounds are real chemical individuals?

4. (*a*) State in your own words the meaning of the chart of equivalents of metals and non-metals.
(*b*) State each of the four quantitative laws of chemical combination.

5. Write your version of the monologue Democritus might have given his pupils on "the atomicity of matter".

6. (*a*) Why was Dalton's problem more difficult than that of Democritus?
(*b*) State concisely Dalton's atomic assumptions.
(*c*) Give your explanation of *each* of the four quantitative laws according to Dalton's theory.

7. How did Dalton's theory lead him to the Law of Multiple Proportions?

8. (*a*) What is meant by the term "atomic weight"?
(*b*) In order to find the atomic weight of each element from the table of equivalent weights, what additional data is needed?

Problems

1. After 0.500 g. of dry potassium chlorate and some ferric oxide has been heated to produce oxygen it is cooled and found to weigh 0.4327 g. How much oxygen was liberated? What law enables you to calculate this amount?

2. If 159.1 g. of a copper sulphide contains 32.06 g. of copper, how much sulphur is needed to combine with 0.6357 g. of copper to make this sulphide? What laws are used in this problem?

3. Find the equivalent weights of the following elements from the combining proportions given:
(*a*) 0.4495 g. of aluminum and 1.773 g. of chlorine.
(*b*) 0.0304 g. of magnesium and 0.0200 g. of oxygen.
(*c*) 1.00 g. of fluorine and 0.053 g. of hydrogen.
(*d*) Sulphur combines with half its weight of oxygen.
(*e*) Zinc combines with 0.49 times its own weight of sulphur.

4. (*a*) Methane is 25% hydrogen and 75% carbon, while ethylene is 14.3% hydrogen and the balance carbon. By calculating the weights of hydrogen combined with 100 g. of carbon show that these compounds illustrate the Law of Multiple Proportions.

(*b*) Complete the following table:

Compound	*% Nitrogen*	*% Oxygen*	*O_2 combined with 28 g. of nitrogen*	*Ratio of wts. of O_2 to one another*
Nitrous oxide	63.65	36.35		
Nitric oxide	46.68	53.35		
Nitrogen trioxide	36.84	63.16		
Nitrogen dioxide	30.44	69.56		
Nitrogen pentoxide	25.94	74.06		

Chapter 9

The Atomic-Molecular Theory

1. Gay-Lussac's Law of Combining Volumes. Dalton provided a method of explaining chemical changes but not a completely satisfactory method of calculating the atomic weights. Others struggled with the problem for the next fifty years before they saw the solution clearly. Many almost found the complete explanation and each of them made an important contribution. We now turn to their struggles, failures and successes.

Cavendish had measured the combining volumes of hydrogen and oxygen, between 1781 and 1784, and had found them to be almost exactly in the ratio of 2:1. Alexander Von Humboldt found the ratio to be the same. Joseph Louis Gay-Lussac confirmed his results and was so impressed with the simplicity of the ratio that he investigated other pairs of gases. His results and those of his followers show that at the same temperature and pressure:

(1) One volume of oxygen combines with two volumes of hydrogen to give two volumes of water (as steam).

(2) One volume of oxygen combines with one volume of nitrogen to give two volumes of nitric oxide.

(3) One volume of oxygen combines with two volumes of nitrogen to give two volumes of nitrous oxide.

(4) One volume of oxygen combines with two volumes of carbon monoxide to give two volumes of carbonic acid gas.

(5) Two volumes of oxygen combine with one volume of nitrogen to give two volumes of nitrogen dioxide.

(6) One volume of nitrogen combines with three volumes of hydrogen to give two volumes of ammonia gas.

(7) One volume of hydrogen combines with one volume of chlorine to give two volumes of hydrogen chloride gas.

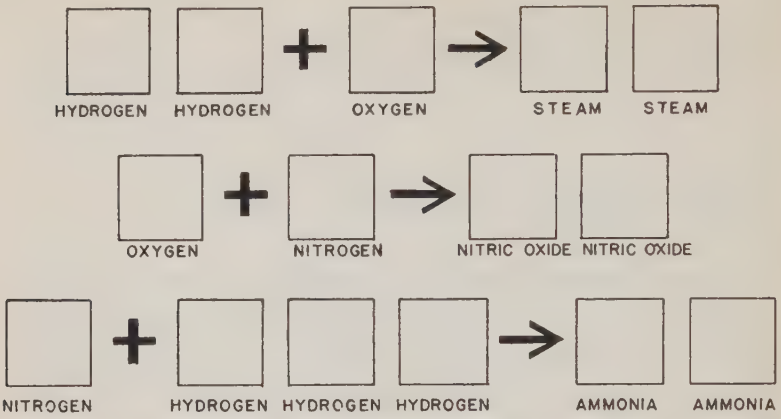


Fig. 51. Gay-Lussac's Law of Combining Volumes.

Some of these volume relationships are shown in Fig. 51.

In 1808 Gay-Lussac made a generalization from these results known as the Law of Combining Volumes. *The volumes of all gaseous substances that take part in a reaction, or are produced by a reaction, are to one another in the ratio of small whole numbers.* Dalton seems to have assumed this could only be true if equal volumes of gaseous substances contain equal numbers of *atoms*. He found two reasons to reject the law. First, his own experiments, which were less exact than those of Gay-Lussac, did not show exact whole number ratios. Second, he pointed out that certain results required the atoms to be divisible. This appeared to be an unresolvable difficulty according to his theory.

2. Avogadro's hypothesis. In 1811, in Italy, Avogadro suggested a solution of the difficulty. He pointed out that the elementary gases might not exist as atoms but as small groups of atoms or small masses. These small masses he called *molecules*. He made the now famous assumption which forms the basis of the atomic-molecular theory: *Equal volumes of all gases at the same temperature and pressure contain equal numbers of molecules.* Gay-Lussac's Law of Combining Volumes could

be used with Avogadro's hypothesis to prove that each molecule contained an even number of atoms.

Explanation of Combining Volumes

Example 1.

(*i*) *Experimental fact.* One volume of oxygen and two volumes of hydrogen form two volumes of water (as steam).

(*ii*) *Assumption.* Equal volumes contain equal numbers of molecules. Let one volume contain n molecules.

(*iii*) *The Reasoning.* n molecules of oxygen combine with $2n$ molecules of hydrogen to give $2n$ molecules of steam. In each of the n cases of combination we may say:

1 molecule of oxygen combines with 2 molecules of hydrogen to give 2 molecules of steam.

Each molecule of steam contains the same amount of oxygen so the molecule of oxygen must be divisible into two parts. We thus say the the oxygen is *diatomic.*

Example 2. Perhaps this explanation will be clearer if you look at the volume diagrams in Fig. 52. Here the unit volume is taken so small that it contains only a dozen molecules. Circular symbols, such as Dalton used, represent the atoms in the various molecules. You should go through the argument which leads to the logical conclusion that each molecule of a gaseous element contains an even number of atoms.

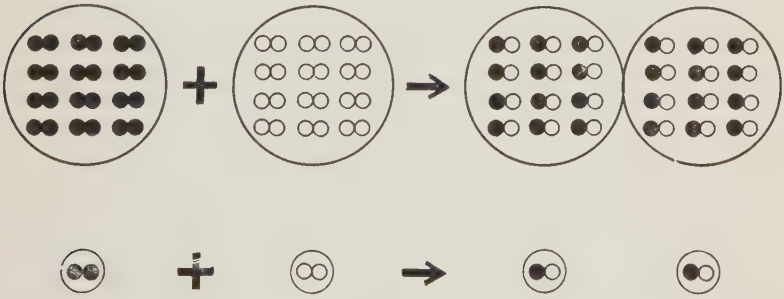


Fig. 52. Why we believe some molecules contain two atoms.

3. Relative molecular weights. The idea of finding the relative weights of two kinds of particles may be illustrated by considering some glass marbles and steel balls of exactly the same size. Suppose you poured a boxful of the glass marbles into the scoop on the grocer's scale and found them to weigh 5 lb. If you then filled the same box to the same

level with the steel balls and weighed them on the grocer's scale you might find them to weigh 15 lb.

Since the balls and the marbles are both the same size you can reason that the same number of each was placed on the scale so each steel ball must be three times as heavy as each glass marble. You do not need to know the number of balls or marbles in the box as long as you know that you have the *same number* of each kind.

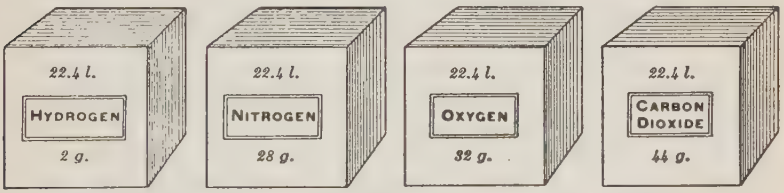
If we think of weighing the hydrogen molecules which fill the box and then the oxygen molecules which fill it, we will know the relative weights of the molecules of hydrogen and oxygen if we are correct in assuming that the box contains equal numbers of molecules each time at the same temperature and pressure. We do not need to know how many molecules are in the box unless we wish to know their individual weights.

You can see that the consequence of Avogadro's hypothesis was that if each unit volume contained the same number of molecules the *ratio of the weights* of the unit volumes would be the same as the ratio of the weights of the individual molecules. If each unit volume contains *n* molecules then the weight of each molecule is 1/*nth* of the weight of the unit volume. Since Avogadro's hypothesis applied to gases and vapours, the relative weights of the molecules of vaporizable substances could thus be found. These weights are called the *molecular weights.* One substance must be chosen as a standard and a number assigned to it. The first substance chosen was hydrogen because it was the lightest gas and it was given unit molecular weight. This was not the best choice for the practical use of the molecular theory.

The standard of reference for molecular weights now used is oxygen and it is given number 32 as its relative weight. We thus have the modern method of obtaining molecular weights from the density of the vapour of volatile substances.

$$\frac{\text{Molecular weight of unknown}}{\text{Molecular weight of oxygen (32)}} = \frac{\text{Weight of any volume of the unknown}}{\text{Weight of an equal volume of oxygen at the same temperature and pressure as that of the unknown.}}$$

A simplification can be made if we use the gas laws to calculate the theoretical volume of the molecular weight of the unknown at standard temperature and pressure (0°C. and 760 mm. of mercury). The volume of oxygen which has a weight of 32 g. at standard temperature and pressure (S.T.P.) is called the *Gram Molecular Volume* and it is 22.4 litres. This name is used because it is the *volume* whose weight in *grams* is the same *number* as the *molecular weight*. It will save us working with the ratio if we simply calculate the weight in grams of 22.4 litres of any volatile substance at S.T.P.



From Black & Conant: "New Practical Chemistry", courtesy The Macmillan Company

Fig. 53. The gram molecular volume (22.4 litres at S.T.P.) always contains a gram molecular weight.

For example: Nitrogen weighs 1.25 g. per litre at S.T.P. Its molecular weight is thus $1.25 \times 22.4 = 28$. The molecular weight is not 28 g. but simply 28. There is a name for the quantity in grams whose weight is the same as the *number* used for the molecular weight. It is called a *mol* (pronounced mole). It has a volume of 22.4 l. at S.T.P. The molecular weights of all substances are thus found by multiplying the vapour densities at S.T.P. by 22.4. This conversion factor can only be used if the vapour density is given in grams per litre.

A molecule is now defined as the smallest particle of a substance which is capable of independent existence.

An atom is defined as the smallest particle of an element which is capable of entering into chemical combination.

4. Cannizzaro's method. A clear-cut method of selecting the atomic weight from the combining weights was still needed. Cannizzaro realized that this need could be met if the molecular weights were chosen so as to make the molecular weight of hydrogen just twice the atomic weight of hydrogen. Cannizzaro used Avogadro's hypothesis as the basis of his system by realizing that all molecular weights of compounds as well as elements must contain the same number of molecules. He described the system he used to teach his students in a pamphlet distributed at a chemical convention in 1858. His system was as follows:

1. Find the molecular weights of as many compounds as possible of a selected element, E. These molecular weights are to be based on a molecular weight of two for hydrogen.
2. By chemical analysis determine the weight of the element, E, in each of the molecular weights.
3. These weights will be either the atomic weight of the element, E, or multiples of it. *The smallest weight of an element ever found in the molecular weight of any of its compounds is its atomic weight.*
4. Certain elements are gases and can be shown to be diatomic by their combining volumes. The atomic weight is then half the molecular weight found from the density of their vapours.

Since his time we have adopted oxygen with a molecular weight of exactly 32.0000 as the standard because it is more abundant than hydrogen, forms more compounds, and makes more of the atomic weights whole numbers. This choice gives hydrogen a molecular weight of 2.016.

The mass spectrometer enables men today to determine the relative weights of extremely small numbers of atoms and molecules with better than five-figure precision and it experimentally verifies what men deduced by simple logical reasoning years ago.

Cannizzaro's method is illustrated by the following table. You will observe that the weights of carbon found in the gram molecular weights of its compounds are 12 grams or multiples of 12 grams.

TABLE 10—CANNIZZARO'S METHOD

Compound	*Density of Vapour g./l. (S.T.P.)*	*Molecular Weight*	*Percentage of carbon*	*Weight of carbon in molecular wt.*
Methane	0.717	16	75%	12
Ethane	1.34	30	80%	24
Propane	1.98	44	82%	36
Ethylene	1.25	28	85.7%	24
Carbon Monoxide	1.25	28	43.0%	12
Carbon Dioxide	1.98	44	27.3%	12

5. Valence. The many equivalent weights for the elements could now be explained. If an element combined with hydrogen or chlorine, atom for atom, its equivalent weight was the same as its atomic weight. It was said to be *univalent* or to have a valence or combining power of 1. If one atom of an element combined with one atom of oxygen or two atoms of hydrogen or chlorine its equivalent weight was then one-half of its atomic weight because it was said to be *divalent* or to have a combining power of 2. Similarly elements were said to have valences of 3 or 4, etc.

The quantitative measure of combining power can now be found. If unit valence is represented by the equivalent weight as it is defined, then the number of equivalent weights in the atomic weight gives the valence. The valence of course is the nearest whole number because atomic weights as found by Cannizzaro's method are not very accurate and will not divide evenly by the precise equivalent weights. The relationship may be formulated:

$$\text{Valence} = \frac{\text{Atomic weight}}{\text{Equivalent weight.}}$$

The precise value of the atomic weight can be found by multiplying the valence (a whole number) by the precise equivalent weight.

The confusion and controversy about atomic weights and atomic theory slowly dissolved away and the stage was set for the great modern drama of chemical development. In

the next two chapters we will try to learn how this theory is applied to the great mass of chemical substances.

6. Avogadro's number. Although the men of a century ago had to be content with the relative weights of atoms and molecules, refinement of measurement and increased knowledge soon made it possible to know the number of molecules in a gram molecular weight. This number has been determined by several independent methods and it is believed to be very close to 6.03×10^{23}, that is, there are 60,300,000,000,000,000,000,000 molecules of oxygen in 32 grams. If you had a pint bottle full of oxygen at S.T.P. and only two hydrogen molecules per second entered and combined with the oxygen, it would be over four hundred million million years before the oxygen was all converted to water. There are 6.03×10^{23} molecules of any substance in a gram molecular weight so this weight is called a *mol*, and this number is called *Avogadro's number*.

One gram atomic weight, 32 grams, contains 6.03×10^{23} atoms of sulphur and the *same is true for each gram atomic* weight of any element. A gram atomic weight of any element is called a *gram atom*, and it has an Avogadro number of atoms.

You can readily see that it is now possible to find the absolute weight of a single molecule or a single atom. Thus a molecule of hydrogen weighs 3.34×10^{-24} grams and an atom weighs 1.67×10^{-24} grams. The absolute weight of other atoms and molecules can be found by multiplying by the relative atomic and molecular weights.

Question Summary

1. State Gay-Lussac's Law of Combining Volumes and show how it is illustrated by the combination of hydrogen and chlorine to produce hydrogen chloride.

2. (*a*) What solution was proposed by Avogadro to the problem in Question 1 above?

(*b*) Show how Avogadro's assumption explains the combination of hydrogen and chlorine.

3. (*a*) How does Avogadro's hypothesis make it possible to determine the relative weights of the molecules of volatile substances?

(*b*) If the molecules of those gases which are elements are diatomic, is there a method independent of combining proportions for determining the relative weights of the atoms? Explain the method.

4. Cannizzaro combined a hypothesis with one of the laws of chemical combination. Name each and show how he did this to determine atomic weights.

5. (*a*) Why are the equivalent weights not always equal to the atomic weights?

(*b*) How is the precise atomic weight of an element found?

6. Suppose one cubic centimetre of water has all its molecules touching one another. What is the maximum volume of a water molecule?

Illustrative Problems

1. If 100 ml. of each of the pairs of gases in the explanation of Gay-Lussac's Law of Volumes were made to react together completely, calculate what volume of unused gas would remain in each of the seven cases listed.

2. Suppose 150 ml. of oxygen and 200 ml. of carbon monoxide were made to combine as completely as possible, what would be the total volume of the final mixture?

3. If the gram molecular volume (G.M.V.) is 22.4 litres at S.T.P., what is the weight of one litre of oxygen at S.T.P.?

4. A certain gas is found to be twice as dense as oxygen at the same temperature and pressure. What is its molecular weight?

5. If one litre of chlorine (atomic weight = 35.5) weighs 3.17 g. at S.T.P., what is its molecular weight? What do you conclude about the number of atoms per molecule?

6. Calculate the molecular weight of each of the following if the weight of 1 litre at S.T.P. is: nitrogen = 1.2506 g.; ammonia = 0.7708 g.; nitric oxide = 1.3402 g.

7. Calculate the weight of 1 litre at S.T.P. of each of the following gases if the molecular weights are: sulphur dioxide = 64; carbon dioxide = 44; marsh gas = 16.

8. Find the weight of 225 ml. of hydrogen chloride at S.T.P. if the molecular weight is 36.5.

9. Find the weight of one molecule of a substance if 400 ml. of it at S.T.P. weighs 0.714 g.

10. How many atoms are there in one milligram of gold?

Chapter 10

Learning Chemical Language

1. Symbols. We have used symbols, formulas and equations from the beginning so that you would become familiar with them and also to make the chapters complete. We now wish to learn how they were evolved and what is their full meaning.

In astrology the sun, moon and the five known planets were represented by symbols. Since the alchemist thought the generation of metallic properties was due to the influence of these bodies he adopted the astrologer's symbols. The yellow gold, which was the noblest of the metals because it resisted the action of Aqua Regia, the royal water, was supposed to be produced by the action of the sun so its alchemical symbol was a modified sun. When the Romans named it they called it Aurum from the Latin word for sun. We use the symbol, Au, derived from this Latin name. Silver, less noble than gold, was connected with the pale moon, Luna, and it had a conventionalized moon for a symbol. Suppliers still call its nitrate *lunar caustic* in some listings. Because of its economic uses the Romans called it Argentum, so we use the symbol, Ag. Mercury was first represented by the Serpent's staff of Hermes, the fleet messenger of the Gods. Its more common name was quicksilver, and the Latin name was Hydrargium or liquid silver, hence the symbol, Hg. Copper was represented by the mirror of Venus, and the Latin name for it was Cuprum, so its modern symbol became Cu. Iron was the metal of weapons so it was related to Mars, and the shield and spear became its symbol. The Latin

name was Ferrum so its symbol is Fe. Lead was represented by the scythe of vast Saturn and was the plumber's metal, hence its Latin name Plumbum with the derived symbol Pb. Tin was supposed to come from the throne of Jupiter and the Romans called it Stannum, so our symbol is Sn.

Inconvenient circular symbols were used even in Dalton's time but in 1802 Thompson proposed the use of literal

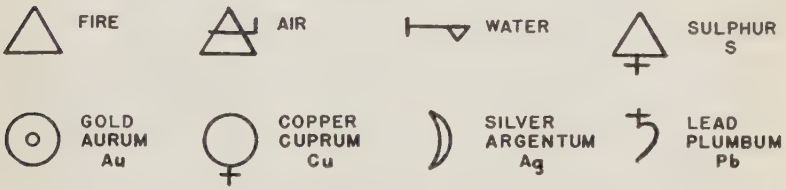


Fig. 54. Some alchemical and modern symbols.

symbols. The international use of the new symbols was foreseen by choosing them so that all nations could understand their meaning. Since Latin was universally understood many of them were taken from the first letter of the Latin name. The first letter is always a capital letter. If another letter is needed to identify the element a small characteristic letter is added. The great Swedish Chemist, Berzelius (1779-1848), did much to facilitate and popularize the use of modern symbols, We thus have C for carbon, Ca for calcium, Cu for copper, Cl for Chlorine, Co for cobalt, Cs for cesium, Ce for cerium and Cr for chromium. O stands for oxygen and Os for osmium. You can find all of them in the table of atomic weights. If you concentrate on learning the names of the elements first, and then noting those whose symbols are derived from ordinary names, you will find it very easy to memorize the few which have been derived from the Latin names. It is wise to pay particular attention to sodium, Latin name *natrium*, potassium called *kalium*, antimony called *stibinum*, magnesium, manganese and mercury.

After the development of the atomic-molecular theory, symbols had a great deal of meaning. A symbol now means three things:

(1) It is a shorthand sign for the element.
(2) It is an atomic symbol and represents one atom.
(3) It represents an atomic weight or 6.03×10^{23} atoms of the element.

2. Formulas. You have seen the symbols used to represent the composition of a compound or the molecule of an element. When there is more than one atom of a certain kind in a compound or molecule we place an arabic numeral after and slightly below the symbol to indicate the number of atoms or groups of atoms in the substance. Thus H_2SO_4 shows that sulphuric acid has hydrogen, sulphur and oxygen in the proportion of two atoms of hydrogen, one atom of sulphur, and four atoms of oxygen in its molecule. This composition is deduced from the percentage composition. The group of symbols which represents a compound or a molecule is called a *Chemical Formula.* Since the symbols represent weights as well as atoms of elements the formula shows the composition by weight. Thus sulphuric acid contains 2.016 g. of hydrogen, 32.06 g. of sulphur and 64 grams of oxygen in 98.076 g. of the pure acid. The percentage composition is calculated from these weights. The sum of the atomic weights represented by a formula is called a *formula weight.*

The formula of a substance thus gives us considerable information:

(1) It shows the elements which are present.
(2) It shows the number of atoms of each kind.
(3) It enables us to find the percentage composition.
(4) In many cases it represents the molecule of a compound or element.

3. Formula weights and molecular weights. You will have to be very careful about the last point regarding formulas because, as we shall learn later, it is very difficult to define

just what is a molecule of a crystalline salt. In the case of many substances the formula only represents the simplest ratio of the elements present and does not define the number of times this unit is repeated in a quantity which might be capable of independent existence. We are always safe in saying that the sum of the atomic weights represented by a formula is a *formula weight*, but it may not be a molecular weight unless the composition of the molecule is known.

Many substances do have very definite molecules under certain conditions and the number of atoms in each is fairly certain. You have seen how we conclude that the molecules of hydrogen, oxygen, nitrogen and chlorine are diatomic. We thus write the formulas of their molecules as H_2, O_2, N_2, Cl_2. Similarly any compound which permits us to determine its molecular weight may be represented by a molecular formula. Most substances except salts have well-known molecular formulas and the sum of the weights of the atoms in the formula is the molecular weight. Thus H_2O is the molecular formula for water in the vapour state, CO_2 is the molecular formula for carbon dioxide, etc. You will gradually learn the formulas of common substances.

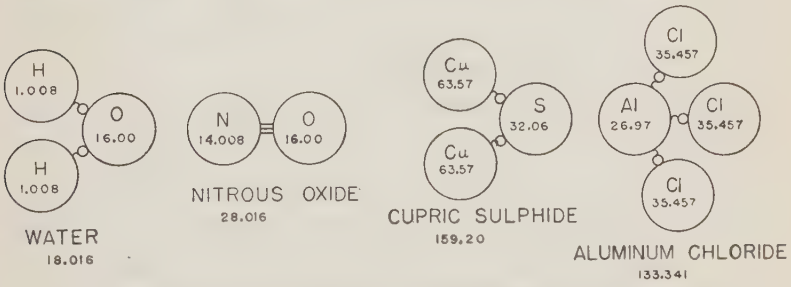


Fig. 55. Formulas give the exact composition of compounds.

4. Radicals. When we wish to indicate more than one molecule or formula weight of a compound or element we write a large arabic numeral in front of the formula or the

symbol. Thus 2 H_2O means two molecules of water or two molecular weights of water. 2 H means two atoms of hydrogen or two atomic weights of hydrogen. When no number appears before or behind a symbol or formula it means that only one atom or molecule is involved. When a *group of atoms behaves as a single atom* we call the group a *radical*. If it behaves like a metal we call it a *metallic radical* and if it behaves like a non-metal we call it a *non-metallic radical*. We often wish to show that a substance contains more than one radical of a certain type so we put brackets around the symbols for the radical. Thus $Ca(OH)_2$ is calcium hydroxide. The OH group is called the hydroxyl radical and calcium hydroxide contains two of these radicals per formula. You will note that in writing formulas we put the metallic elements, metallic radicals and hydrogen first, and the non-metallic elements and radicals at the end. The OH group is an example of a non-metallic radical. You will note that the number of radicals is indicated by a numerical subscript. Thus $Al_2(SO_4)_3$ is aluminum sulphate because the percentage composition is such as to require three sulphate radicals for each two aluminum atoms. The most common metallic radical is the ammonium radical, NH_4. For example $(NH_4)_2SO_4$ is ammonium sulphate which has two ammonium radicals for each sulphate radical.

5. Valence and formulas. Valence is the key to writing correct formulas. There are many ways to find the valence of an element from very common compounds. The simplest method is to remember the formulas of the so-called hydrides or hydrogen compounds of the non-metallic elements. *Since hydrogen is the unit of combining power it has a valence of 1.* The formula shows the combining power of the other element. Four valences are shown in:

HI	H_2S	PH_3	CH_4
hydrogen iodide,	hydrogen sulphide,	phosphine,	methane.

Iodine is monovalent here because it combines with one hydrogen atom and its equivalent weight equals its atomic weight. Sulphur is divalent, phosphorous is trivalent and carbon is tetravalent.

Oxygen has a valence of 2 except in the peroxides. Most metals and non-metals form well-known oxides and their valence may be determined by this rule. You must be careful of this rule because two oxides of a metal may combine together to form a molecular compound. Thus iron forms 2 oxides, FeO, ferrous oxide, and Fe_2O_3, ferric oxide. The valence of iron in the first is 2 and in the second it is 3. These two oxides are equivalent to the oxide Fe_3O_4, iron rust, but the existence of this oxide does not mean a fractional valence for iron but only an appearance of such a valence. With a very few exceptions the oxides reveal the valence of the element readily. PbO is lead oxide or litharge. PbO_2 is lead dioxide. There is a Pb_3O_4 called red lead or minium which is equal to 2 PbO. PbO_2. The peroxides are particularly deceiving. Na_2O is sodium oxide and it shows that the valence of sodium is 1. However, there is another oxide, Na_2O_2, called sodium peroxide and one of its oxygen atoms is attached in such a way that it appears to have no valence, so the valence of sodium is 1. Many chemists like to distinguish between valence (the force) and valence number as calculated by the above rule. *The valence force always exists in whole number units* but its average numerical value for an element in a compound may appear to be a fractional value. These valence numbers have no physical significance but they are useful in the balancing of equations. You will learn more about valence in Chapter 32.

6. Valence of metals and non-metals. It is hoped that the following classification of elements and radicals into metallic and non-metallic divisions of progressively greater valence may help you in writing correct formulas. The list

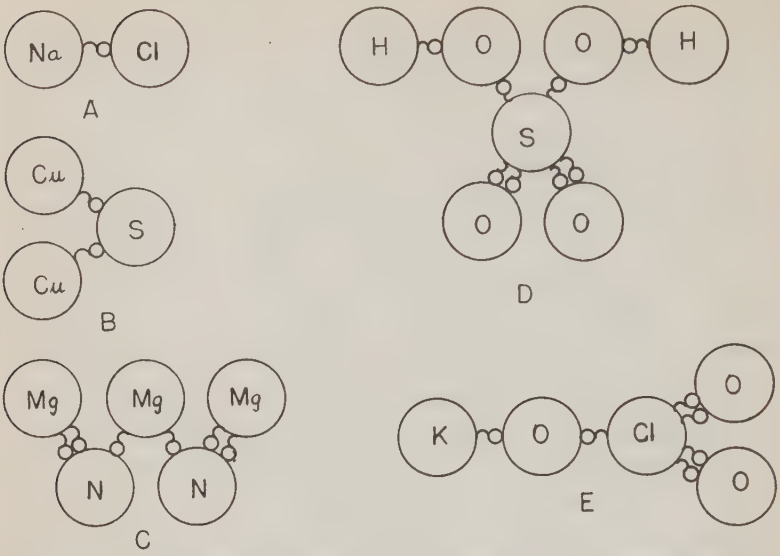


Fig. 56. The valence of elements in compounds. A, monovalent elements; B, monovalent copper and divalent sulphur; C, divalent magnesium and trivalent nitrogen; D, monovalent hydrogen, divalent oxygen and hexavalent sulphur; E, pentavelent chlorine.

does not pretend to be complete but it shows the commonest valences of some of the more important elements and radicals. When an element or radical has a valence of 1 it is said to be monovalent or univalent. When its valence is 2 it is divalent or bivalent. If it is 3 we call it trivalent or tervalent; if 4, quadrivalent or tetravalent; if 5, quinquivalent or pentavalent; if 6, sexivalent or hexavalent; if 7 heptavalent; and when it has a valence of 8 we call it octavalent. The names in the table are those used in naming the salts.

7. Nomenclature. The naming of chemical compounds is called Nomenclature. The following rules and explanations may help you. You should do the exercises after each rule.

A. Naming of inorganic acids and salts.

Rule 1. Binary *acids* (only *two* different elements) all have the prefix "hydro-" for hydrogen and the suffix "ic", indicating the ordinary valence state. HF is hydrofluoric acid.

Name the following acids: HCl, HBr, HI, H_2S, HCN.

TABLE 11—COMMON VALENCES

Valence Type	*Metallic*		*Non-metallic*	
I. Monovalent or Univalent (valence of 1.)	Hydrogen	H	Fluoride	F
	Lithium	Li	Chloride	Cl
	Sodium	Na	Bromide	Br
	Potassium	K	Iodide	I
	Ammonium	NH_4	Hydroxide	OH
	Cuprous	Cu	Nitrate	NO_3
	Silver	Ag	Nitrite	NO_2
	Mercurous	Hg	Chlorate	ClO_3
			Acetate	$C_2H_3O_2$
II. Divalent or Bivalent (valence of 2.)	Magnesium	Mg	Carbonate	CO_3
	Calcium	Ca	Sulphate	SO_4
	Strontium	Sr	Sulphite	SO_3
	Barium	Ba	Sulphide	S
	Zinc	Zn	Oxide	O
	Cadmium	Cd	Silicate	SiO_3
	Mercuric	Hg	Peroxide	O_2
	Stannous	Sn	Chromate	CrO_4
	Lead	Pb		
	Cupric	Cu		
	Ferrous	Fe		
III. Trivalent or Tervalent (valence of 3.)	Aluminum	Al	Phosphate	PO_4
	Ferric	Fe	Phosphite	PO_3
	Arsenic	As	Arsenite	AsO_3
	Antimony	Sb	Arsenate	AsO_4
	Bismuth	Bi	Nitrogen in NH_3	
IV. Tetravalent or Quadrivalent (valence of 4.)	Stannic	Sn	Sulphur in SO_2 Carbon in CO_2 or CH_4	
V. Pentavalent or Quinquivalent (valence of 5.)	Antimony	Sb	Nitrogen in N_2O_5	
	Bismuth	Bi	Phosphorus in P_2O_5	
VI. Hexavalent or Sexivalent (valence of 6.)	Chromium in CrO_3		Sulphur in SO_3	
VII. Heptavalent (valence of 7.)			Chlorine in $HClO_4$	
VIII. Octavalent (valence of 8.)	Osmium in OsF_8			

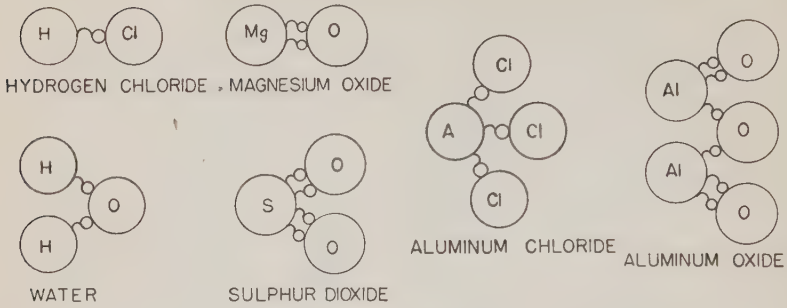


Fig. 57. The naming of compounds from formulas.

Rule 2. The names of other binary compounds consist of the name of the metal, then that of the non-metal or radical with the suffix "ide". CN (cyanide) and OH (hydroxide) are named as elements.

Example: NaCl is sodium chloride.

Name the following compounds: $CaCl_2$, $BaBr_2$, Na_2S, SrO, K_2F_2, Hg_2Cl_2, HgI_2, KCN, MgH_2, $FeCl_3$, FeS, Cu_2S, CuO, Bi_2S_3.

Rule 3. When an acid or a salt has three different elements it is said to be *ternary*. Thus H_3PO_3 (phosphorous acid) is a ternary acid and Na_3PO_3 (sodium phosphite) is a ternary salt.

(*i*) In the naming of ternary acids the suffix "ic" is used for the supposedly common valence state. Thus $HClO_3$ is chlor*ic* acid. The suffix "ous" is used on the next lower valence state or valence number. Thus $HClO_2$ is chlor*ous* acid. A valence number higher than that indicated by the "ic" suffix uses the prefix "*per*"—as well as the suffix; $HClO_4$ is *per*chlor*ic* acid. A valence number less than that indicated by the "ous" ending uses the prefix "hypo-" as well as the suffix; HClO is *hypo*chlor*ous* acid. The formula of the "ic" acid of each element has to be memorized.

(*ii*) Ternary salts use the suffix "ate" to replace the "ic" used in names of acids and the suffix "ite" to replace the "ous" used. Thus $KClO_3$ is potassium chlorate and $Ca(ClO)_2$ is calcium hypochlorite. The "per-" and "hypo-" prefixes are used as before.

Name the following acids and salts: $HBrO_3$, $KBrO_4$, H_2SO_4, $PbSO_4$, HNO_3, H_3PO_4, HCNO, KCNO, H_2CO_3, $KMnO_4$.

Rule 4. The "ous" ending for the lower valence state and the "ic" ending for the higher valence state of metals is used in both binary and ternary compounds.

Examples:

Hg_2Cl_2—mercurous chloride (calomel)

$HgCl_2$—mercuric chloride (corrosive sublimate of mercury)

Cu_2O—cuprous oxide (red copper oxide)

CuO—cupric oxide (black copper oxide)

$FeSO_4$—ferrous sulphate

$Fe_2(SO_4)_3$—ferric sulphate

There are some prefixes such as "meta-", "ortho-" and "pyro-" which are best learned later. The prefix "thio-" is used to indicate that an atom of sulphur replaces an atom of oxygen in a compound; Na_2SO_4 is sodium sulphate; $Na_2S_2O_3$ is sodium thiosulphate. Nothing but an immense amount of attentive practice will fix the valences and names in the mind. Perhaps the summary in Table 12 will help you with the naming of the more common acids and salts.

TABLE 12—THE NAMING OF ACIDS AND SALTS

Acids		*Salts*
Hydro	ic	..... ide
.....	ous	..... ite
.....	ic	..... ate

Examples:

HCl —Hydrochloric acid.	NaCl —Sodium chloride.
$HClO_2$—Chlorous acid.	$NaClO_2$—Sodium chlorite.
$HClO_3$—Chloric acid.	$NaClO_3$—Sodium chlorate.

8. Writing formulas from names. Let us see how the knowledge of valences and names will enable us to write formulas.

Elementary principle: When two elements or radicals which have the same valence unite to form a compound they combine unit for unit.

Examples:

(*i*) Li and F $\longrightarrow$ LiF (lithium fluoride)
Na and Cl $\longrightarrow$ NaCl (sodium chloride)

(*ii*) Mg and SO_4 $\longrightarrow$ $MgSO_4$ (magnesium sulphate)
Zn and CO_3 $\longrightarrow$ $ZnCO_3$ (zinc carbonate)

(*iii*) Al and PO_4 $\longrightarrow$ $AlPO_4$ (aluminum phosphate)

General principle: When two elements or radicals unite to form a compound *the total metallic valences will equal the total non-metallic valences.*

Examples:

(*i*) 2 H and O $\longrightarrow$ H_2O (water)
Ba and 2 Cl $\longrightarrow$ $BaCl_2$ (barium chloride)
Al and 3 OH $\longrightarrow$ $Al(OH)_3$ (aluminum hydroxide)

(*ii*) 2 Al and 3 O $\longrightarrow$ Al_2O_3 (aluminum oxide or alumina)

When odd and even numbers are involved it is easier to find the least common multiple of the valences. In the case of aluminum oxide it is 6, since the valences are 2 and 3. Two atoms of aluminum have a metallic valence of 6 and 3 atoms of oxygen have the same valence but they are non-metallic. The molecule as a whole is neutral. We can make a rule, metallic and non-metallic atoms and groups of atoms being often called radicals as a single descriptive term.

$$\begin{matrix}\text{Number of metallic} \\ \text{radicals} \times \text{valence}\end{matrix} = \begin{matrix}\text{number of non-metallic} \\ \text{radicals} \times \text{valence}\end{matrix} = \begin{matrix}\text{L.C.M. of} \\ \text{valences.}\end{matrix}$$

The beginner should try to learn the symbols and valences of those common elements which have only one valence in binary compounds. The number of possible combinations of metallic and non-metallic elements would make it prohibitive to learn the formulas. It would also be foolish to try to write them all out because many combinations do not give stable compounds or at best very rare compounds. Formulas represent the percentage compositions of known compounds and we will simply have to learn about these as we study the story of matter.

Question Summary

1. Describe briefly the derivation of the following symbols: Au, Cu, Ag, Hg, Sn, Pb, Fe, Na, K, Sb.

2. Name three things a symbol tells us.

3. Can we have a formula for an element? Explain. Can we have a symbol for a compound in our modern system? Explain.

4. What is the difference between Cl_2 and 2 Cl; between $Al(OH)_3$ and H_3AlO_3; between a molecular weight and a formula weight?

5. Define valence and describe briefly how it is obtained by the inspection of known formulas.

6. Can an element have more than one valence? Give examples.

7. Name some things we can learn from the formula of a compound. What does $Ca_3(PO_4)_2$ tell you?

8. Describe briefly with examples how the correct formulas may be written from the names of compounds.

Problems and Exercises

1. Write from memory the names of the elements with the following symbols: Mg, K, Cl, Na, Ca, Mn, Cr, S, Br, Hg, Be, Li, He, Co, Sn, Pb, Cu, Sb.

2. Write from memory the symbols of the elements mentioned in the Table of Contents of this book.

3. Make a new table of the valences of the common elements and radicals. Write metals, non-metals and radicals as horizontal headings, and univalent, divalent, trivalent, etc. as vertical groupings.

4. List the common metallic elements in a horizontal row about two inches apart across the top of several pages of your notebook. List the common non-metallic elements and radicals on every second line in the margins. Write in the correct formula and the name wherever the compound of the elements seems likely to exist.

5. Name each of the following and state the meaning of each number and letter: $3Ca(OH)_2$, $(NH_4)_3PO_4$, $6HNO_3$, NH_3, Na_2O_2, $FeCl_2$, $Fe_2(SO_4)_3$, Cu_2S, Hg_2Cl_2, P_4.

Chapter **11**

Calculations with the Atomic-Molecular Theory

1. Introduction. The atomic-molecular theory and the gas laws are the basis of a great body of quantitative theory by means of which many predictions of chemical results may be made. We wish to summarize these principles for you and to show you how they are applied to the solution of a number of simple problems.

2. Calculation of relative atomic weights. These are made from combining proportions when it is known how many atoms of each kind are involved. For example it is known that hydrogen and chlorine combine in the ratio of 1 atom of hydrogen to 1 atom of chlorine. If 2.016 g. of H_2 combine with 70.91 g. of Cl_2, what is the ratio of the weights of these two atoms? The chlorine atom is $\frac{70.91}{2.016} =$ 35.17 times as heavy as the hydrogen atom. If we take the unit weight of hydrogen as 1.008 g. then the unit weight of chlorine is $35.17 \times 1.008 = 35.457$.

If the combining proportions of hydrogen and oxygen are 1: 7.94 or 2: 15.88, and it is known that two atoms of hydrogen are combined with one atom of oxygen, the relative weight of *one* hydrogen to *one* oxygen atom is 1 : 15.88, so oxygen is 15.88 times as heavy as hydrogen. If the unit weight of oxygen is taken as 16.000 then the unit weight of hydrogen is $\frac{16.000}{15.88} = 1.0076$. More recent values of the ratio make the atomic weight 1.008.

3. Calculation of equivalent weights. The gram equivalent weight is the weight which represents unit valence or unit combining power. For elements:

$$\text{Gram equivalent weight} = \frac{\text{Atomic weight in grams}}{\text{valence.}}$$

We will use the term equivalent weight for gram equivalent weight. If an element exerts more than one valence in different compounds it has more than one equivalent weight. The gram equivalent weight is *defined* as the weight which combines with or displaces 1.008 g. of hydrogen or its equivalent in oxygen (8.000 g.) or chlorine (35.457 g.).

For example: If 1.52 g. of a metal displaces 0.126 g. of H_2 from an acid, what is its equivalent weight?

1.008 g. of hydrogen are displaced by 1 equivalent weight of metal.

0.126 g. of hydrogen are displaced by 1.52 g. of metal.

1.008 of hydrogen is displaced by $1.52 \times \frac{1.008}{0.126} = 12.16$ g. of metal. This is the equivalent weight of the metal.

You might like to use an unknown and set up a ratio. Let x = the equivalent weight. Then

$$\frac{x}{1.52} = \frac{1.008}{0.126}$$

$$x = 1.52 \times \frac{1.008}{0.126} = 12.16 \text{ g.}$$

4. Precise atomic weights from equivalent weights. Since

$$\text{Atomic weight} = \text{Equivalent weight} \times \text{Valence}$$

we can use two steps.

Example: The equivalent weight of tin in very pure stannic oxide is 29.675 g. Calculate the valence and the precise atomic weight if the approximate atomic weight is 111.5.

Step I. Find the valence (a whole number).

$$\text{Valence} = \frac{\text{Atomic weight}}{\text{Equivalent weight}} = \frac{111.5}{29.675} = 3.75$$

The nearest whole number is 4, so the valence of tin in stannic oxide is 4.

Step II. Find the precise atomic weight.

$$4 \times 29.475 = 118.70$$

The correct atomic weight is 118.70.

5. How to think in chemical unit weights. Since each atomic weight in grams contains the Avogadro number, 6.03×10^{23} atoms, it is useful to express all gram quantities of elements in these larger units. A short name for an atomic weight in grams is a gram atom. For example, if we take 10 g. each of carbon, oxygen and hydrogen we have equal weights but not equal numbers of atoms. Thus we have $\frac{10}{12}$ of a gram atomic weight of carbon, $\frac{10}{16}$ of a gram atomic weight of oxygen and $\frac{10}{1.008}$ gram atomic weights of hydrogen. By comparing the number of gram atomic weights we compare the relative numbers of atoms.

6. Calculation of simplest formulas from percentage composition. A formula uses symbols to represent the relative number of atoms of each kind required to represent the analytical composition of a compound. It may represent the composition of the independent particles of an element, e.g., P_4.

Example 1. Suppose a compound is 40% calcium, 12% carbon and 48% oxygen. What is its simplest formula?

Step I. Represent the percentages by gram quantities. In 100 g. of this calcium compound there are: 40 g. of calcium, 12 g. of carbon, 48 g. of oxygen.

Step II. Represent the quantities in gram atom units.

Thus 40 g. of calcium is $\frac{40}{40} = 1$ gram atom of calcium.

12 g. of carbon is $\frac{12}{12} = 1$ gram atom of carbon.

48 g. of oxygen is $\frac{48}{16} = 3$ gram atoms of oxygen.

Step III. The ratio of the number of gram atoms to one another is 1:1:3.

Only the simplest formula may be calculated from the percentage composition alone. The simplest formula is thus $CaCO_3$ since it shows this ratio of gram atoms in symbols.

Example 2. The percentage composition of a salt is: potassium 31.9%, oxygen 39.2% and chlorine 28.9%. What is its simplest forumla?

Step I. The weights in 100 g. of the compound are: potassium 31.9 g., oxygen 39.2 g., chlorine 28.9 g.

Step II. The ratio of gram atoms is:

Potassium: $\frac{31.9}{39.1} = 0.816$ g. atoms per 100 g.

Oxygen: $\frac{39.2}{16.00} = 2.45$ g. atoms per 100 g.

Chlorine: $\frac{28.9}{35.457} = 0.815$ g. atoms per 100 g.

Step III. The ratio of the number of atoms is:
0.816 : 2.45 : 0.815.

This may be simplified by dividing by the smallest number, namely 0.815. It is thus 1 : 3 : 1, if we take the nearest whole numbers. The ratio of atoms is K_1, O_3, Cl_1, or in more familiar form $KClO_3$.

7. Percentage composition from formulas. The analytical labours of many hundreds of men and women over the years have identified thousands of chemical substances as compounds of known formulas. Many of these formulas can be written directly from the names of the compounds and many are listed in handbooks and tables. Since the formula gives the composition in symbols or chemical unit weights it is easy to express it in ordinary percentages.

Example: What is the percentage composition of carbon dioxide?

Step I. Write the correct formula—CO_2.

Step II. Insert weights for symbols—$12 + (2 \times 16)$.

Step III. Find the formula weight—44.

Step IV. Find the fraction each element represents,

Carbon $= \frac{12}{44} \times 100 = 27.27\%$

Oxygen $= \frac{32}{44} \times 100 = 72.73\%$

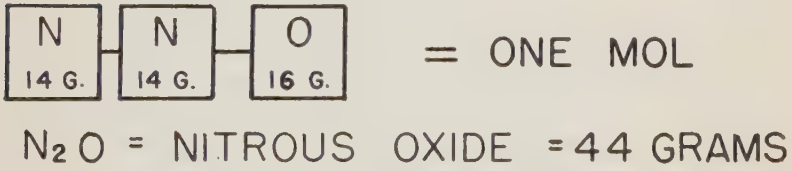


Fig. 58. A mol is a chemical unit quantity.

8. Molecular weights from gas densities at S.T.P. You will recall that the volume of one mol of a vaporizable substance at standard temperature and pressure is 22.4 litres. The manner of calculating molecular weights is very simple.

Example: 250 ml. of a gas at S.T.P. weighs 0.7234 g. Find its molecular weight.

Step I. Find the weight of a litre at S.T.P.

$\frac{1000}{250} \times 0.7234$ g. $= 2.8936$ g.

Step II. Find the weight of 22.4 l. at S.T.P.
22.4×2.8936 g. $= 64.817$ g.
64.817 g. is the weight of one mol.
The molecular weight is 64.817.

9. Molecular weights from relative densities. We may use the principle of relative weights directly.

$$\frac{\text{Molecular weight of an unknown}}{\text{Molecular weight of oxygen (32)}} = \frac{\text{Weight of a fixed volume of unknown}}{\text{Weight of the same volume of oxygen under the same conditions.}}$$

Example: An evacuated glass bulb weighs 16.3452 g. The bulb filled with oxygen at 20°C. and 710 mm. pressure weighs 16.4882 g. and filled with a vapour of unknown molecular weight at the same temperature and pressure it weighs 16.5972 g. Find the molecular weight of the vapour. To find the molecular weight of the vapour let it be x.

$$\text{Now } \frac{x}{32} = \frac{16.5972 - 16.3452}{16.4882 - 16.3452}$$

$$\therefore \quad x = 32 \times \frac{.2520}{.1430} = 56.39$$

Any gas whose molecular weight is well known could be used instead of oxygen as a reference gas.

10. Molecular weight from density of a vapour at any temperature and pressure. The weight of 22.4 litres of the substance as a gas at 0°C. and 760 mm. pressure may be calculated from the weight of any volume of the vapour at any temperature and pressure where it behaves as an ideal gas.

Example: If 100 ml. of the vapour of the substance above was found to weigh 0.354 g. at 27°C. and 720 mm. pressure, you may calculate the vapour density, as follows:

Step I. Correct the volume of the known mass (0.354 g.) to S.T.P. by means of the gas laws.

$$100 \times \tfrac{273}{300} \times \tfrac{720}{760} = 86.2 \text{ ml.}$$

Step II. Calculate the weight of 1 litre at S.T.P.

$$\tfrac{1000}{86.2} \times 0.354 = 4.10 \text{ g.}$$

Step III. Calculate the molecular weight or the weight of the gram molecular volume, 22.4 litres.

$$22.4 \times 4.10 = 91.84.$$

11. Calculation of the molecular formula from the percentage composition and the molecular weight. If we

know the weight of the Avogadro number of molecules and the percentage composition we may calculate the molecular formula. This may be the same as the simplest formula or a multiple of it. The ratio of the number of atoms must be the same in both formulas.

Example: A gaseous compound contains 92.26% carbon and 7.74% hydrogen, 250 ml. of the gas at 20°C. and 740 mm. pressure weigh .257 g. Find the molecular formula.

Consider 100 g. of the compound.

Step I. Calculate the simplest formula.

(*i*) Gram atoms of carbon $= \frac{92.26}{12.01} = 7.68$

(*ii*) Gram atoms of hydrogen $= \frac{7.74}{1.008} = 7.68$

(*iii*) Atoms of carbon : atoms of hydrogen

7.68 : 7.68

(*iv*) Simplest ratio = 1 : 1

(*v*) Simplest formula = CH.

Step II. Formula weight of simplest formula

12.01 + 1.008 = 13.018

Step III. Calculate the molecular weight (see sec. 10).

(*i*) $250 \times \frac{273}{293} \times \frac{740}{760} = 221.7$ ml. at S.T.P. weigh 0.257 g.

(*ii*) Weight of one mol $= \frac{22,400}{221.7} \times .257$ g. = 25.97 g.

Step IV. The molecular formula must be a multiple of the simplest formula.

$\frac{25.97}{13.018} = 2$ (nearest whole number)

Molecular formula is C_2H_2.

Alternative method.

Step I. Calculate the gram molecular weight (see Step III above).

Gram molecular weight = 25.97 g.

Step II. Calculate the weight of each element in the molecular weight.

Weight of carbon in a molecular weight

$\frac{92.26}{100} \times 25.97 = 23.96$ g.

Weight of hydrogen in a molecular weight

$\frac{7.74}{100} \times 25.97 = 1.997$ g.

Step III. Calculate the number of gram atoms of each element in a molecular weight.

Gram atoms of carbon in a molecular weight

$\frac{23.96}{12.01} = 1.995$ (approx. 2)

Gram atoms of hydrogen in a molecular weight

$\frac{1.997}{1.008} = 1.985$ (approx. 2)

Step IV. Represent the gram-atom composition by symbols. The nearest whole number of symbols in each case is used. The molecular formula is C_2H_2.

12. The vapour density from the molecular weight. This is much more frequently required and is the reverse of sec. 8. Since the gram molecular weight is the weight of 22.4 litres then the vapour density at S.T.P is

$$\frac{\text{Molecular weight in grams}}{\text{22.4 litres.}}$$

Example: Find the vapour density of ethylene, C_2H_4.

Step I. The molecular weight is 2 (12) + 4 (1.008) = 28.032.

Step II. The density is $\frac{28.032}{22.4}$ g. = 1.251 g./litre.

13. Volume of any weight of a gas. This is the reverse of section 10 so we first calculate the volume at S.T.P. of the given weight, upon the principle that the volume at S.T.P. of 1 mol equals 22.4 litres.

Example: Find the volume of 1 g. of oxygen when measured at 27°C. and 600 mm. pressure.

Step I. Calculate the fraction of a mol.
1 g. of oxygen is $\frac{1}{32}$ mol.

Step II. One mol is 22.4 litres at S.T.P.
$\frac{1}{32}$ mol is $\frac{1}{32} \times 22.4 = 0.7$ litres at S.T.P.

Step III. Correct for the temperature and pressure.

(*i*) 27°C. or 300°A. is warmer than 0°C. or 273°A., therefore the volume will be larger.

(*ii*) 600 mm. pressure is less than 760 mm. pressure so the pressure decrease will increase the volume.

(*iii*) The volume of 1 g. of oxygen at 27°C. and 600 mm. pressure is:

$$0.7 \times \frac{300}{273} \times \frac{760}{600} = 0.974 \text{ litres.}$$

14. Atomic weights by displacing hydrogen. All the principles of chemical calculations using the gas laws and equivalent weights are illustrated by this fundamental method.

Example: Suppose 0.465 g. of a metal displaced 47.5 ml. of hydrogen from an excess of acid. The hydrogen was collected over water at 19°C. and the barometric pressure was 753.6 mm. of Hg. If the vapour pressure of water at 19°C. is 16.6 mm. of Hg what is the equivalent weight of the metal? If its approximate atomic weight is known to be 25 find its valence and atomic weight.

Step I. Find the volume of dry hydrogen at S.T.P.

$$47.5 \times \frac{273}{292} \times \frac{(753.6 - 16.6)}{760} = 43.07 \text{ ml. at S.T.P.}$$

Step II. The weight which will displace 1.008 g. of hydrogen is the equivalent weight. Since 1.008 g. of hydrogen is $\frac{1.008}{2.016} \times 22.4 = 11.2$ litres at S.T.P. the weight which will displace 11.2 litres at S.T.P. is the equivalent weight of the metal. It is $\frac{11,200}{43.07} \times 0.465$ g. $= 12.093$ g.

Step III. The valence is $\frac{25.21}{12.093} = 2$ (to nearest whole number.)

Step IV. The precise atomic weight is
$2 \times 12.093 = 24.186$.

This is a fundamental method but not a very precise method because of the difficulties of measuring gas volumes.

15. Atomic weights by combining proportions with other elements. The precise equivalent weights of other elements besides hydrogen are well known and those of oxygen or chlorine are often used. The equivalent weight of oxygen is 8.000 g. and this is $\frac{8.000}{32.000} \times 22.4$ litres or 5.6 litres at S.T.P. The volume of the equivalent weight of chlorine is one-half of 22.4 litres, or 11.2 litres, because chlorine is diatomic and univalent like hydrogen.

Example: 1.495 g. of antimony were burned in chlorine gas and 356 ml. of chlorine were used up at 21°C. and 950 mm. pressure. Find the equivalent weight and valence of antimony. The atomic weight of antimony is 121.76.

Step I. The volume of chlorine at S.T.P. is
$356 \times \frac{273}{294} \times \frac{950}{760} = 413.2$ ml.

Step II. The equivalent weight of antimony is
$\frac{11,200}{413.2} \times 1.495 = 40.52$ g.

Step III. The valence is $\frac{121.76}{40.52} = 3$ (to nearest whole number).

Problem Summary

1. Summarize the principles used in calculations with the atomic-molecular theory.

2. (*a*) Silver chloride is 75.263% silver. If the atoms combine in a one to one ratio find the relative weights of silver and chlorine, taking chlorine as 35.457.

(*b*) Silver iodide is 45.945% silver. If the atoms combine in a one to one ratio find the relative weight of iodine on the same basis as in Question 2.

(*c*) Barium chloride is 65.952% barium. Two atoms of chlorine are united with one of barium. Find the relative weight of barium on the same basis as above.

3. (*a*) In the combination of hydrogen and oxygen to form water 4.032 g. of hydrogen combine with 32.000 g. of oxygen. What is the equivalent weight of oxygen?

(*b*) In the combination of hydrogen and chlorine 70.914 g. of chlorine combine with 2.016 g. of hydrogen. What is the equivalent weight of chlorine?

(*c*) In the displacement of hydrogen by tin, 118.7 g. of tin displaces 2.016 g. of hydrogen. What is the equivalent weight of tin?

(*d*) If 1.0788 g. of aluminum displaced 0.12096 g. of hydrogen find its equivalent weight.

(*e*) If 1.0897 g. of zinc combined with chlorine to give 2.2716 g. of zinc chloride find the equivalent weight of zinc.

(*f*) If silver oxide is 6.904% oxygen find the equivalent weight of silver.

(*g*) If sulphur dioxide is 49.90% oxygen find the equivalent weight of sulphur.

4. (*a*) A sample of corrosive sublimate of mercury was purified and analysed. In it 2.866 g. of mercury were combined with 1.0131 g. of chlorine. Find the valence by using 200 as the approximate atomic weight of mercury and calculate the precise atomic weight.

(*b*) A metallic oxide contains 59.95% of the metal. If its approximate atomic weight is 48 find the valence and the precise atomic weight of the metal.

(*c*) An oxide of copper contains 89.4% copper. Use an atomic weight of 60 to find the precise atomic weight.

5. (*a*) Alcohol has 24 g. of carbon, 16 g. of oxygen and 6.048 g. of hydrogen in a gram molecular weight. How many atomic weights of each element are present in a molecular weight?

(*b*) How many gram atomic weights of the following elements are represented by 1 gram of each element: bismuth, boron, chromium, zinc, lithium?

6. (*a*) Water is 11.19% hydrogen and the balance oxygen. Calculate the simplest formula.

(*b*) Sulphuric acid is 2.055% hydrogen, 32.69% sulphur, and the balance oxygen. Calculate the simplest formula.

(*c*) A compound is 2.13% hydrogen, 52.75% arsenic, and the balance oxygen. Find its simplest formula.

7. (*a*) Calculate the percentage composition of sodium hydroxide, NaOH, and of zinc arsenate, $Zn_3(AsO_4)_2$.

(*b*) Calculate the percentages of magnesium, sulphur, and water in $MgSO_4.7H_2O$.

(*c*) Calculate the percentages of sodium, iron, nitric oxide and cyanide in sodium nitro-prusside, $Na_2FeNO(CN)_5$.

8. (*a*) One litre of a gas at S.T.P. weighs 4.302 g. Calculate its molecular weight.

(*b*) If 200 ml. of a vapour at S.T.P. weighs 1.066 g., find its molecular weight.

(*c*) If 3240 ml. of a gas at S.T.P. weighs 6.5 grams find its molecular weight.

9. An evacuated glass bulb is found to weigh 14.0337 g. It weighs 14.3674 g. when filled with air whose molecular weight may be taken as 29.0, and 14.6341 g. when filled with an unknown gas. Find the molecular weight of the unknown.

10. (*a*) 960 ml. of a gas at 25°C. and 750 mm. pressure weighs 1.240 g. What is the molecular weight?

(*b*) 0.687 g. of a substance has a volume of 167 ml. measured over water at 91°C. and 1496 mm. of mercury. Find its molecular weight.

11. (*a*) A compound whose molecular weight is 243 is 29.26% chlorine, 65.80% bromine and the balance is carbon. Find its molecular formula.

(*b*) A compound is 29.09% sodium, 40.55% sulphur, and the balance oxygen. Its molecular weight is not precisely defined. How would you write its formula?

(*c*) A compound is 7.74% hydrogen and 92.26% carbon. 300 ml. of the gas at 79°C. and 740 mm. pressure weighs 0.771 g. Find the molecular formula.

12. (*a*) Find the vapour density of nitrogen, N_2; chloroform, $CHCl_3$; and phosphine, PH_3.

(*b*) Find the weight of one litre of the following gases at S.T.P.: ammonia, NH_3; methane, CH_4; carbon dioxide, CO_2.

13. (*a*) What is the volume at S.T.P. of 5 g. of nitrous oxide, N_2O; of 0.3 g. of acetylene, C_2H_2?

(*b*) What volume will 0.2001g. of helium occupy at 27°C. and 700 mm. pressure if the gas is monatomic?

(*c*) What volume will 1.506×10^{20} molecules of propane, C_3H_8, occupy at 91°C. and 600 mm. pressure?

14. 0.3269 g. of a metal, whose approximate atomic weight is 62, liberated 168 ml. of hydrogen from an excess of acid. The hydrogen was collected over water at 29°C., where the water vapour pressure is 30 mm. of Hg and the barometric pressure was 590 mm. of Hg. Calculate the equivalent weight, the valence and the precise atomic weight of the metal.

15. (*a*) Exactly 1.000 g. of silver oxide, Ag_2O, was heated, and 95 ml. of oxygen was produced at 182°C. and 644 mm. pressure. What is the equivalent weight of silver?

(*b*) A flask contained 840 ml. of chlorine at 0°C. and 912 mm. pressure. After 0.6088 g. of antimony was exposed to the chlorine and the temperature returned to 0°C. the pressure was only 760 mm. If all the antimony combined with the chlorine find the equivalent weight of antimony.

Chapter 12

Equations and Calculations

1. Introduction. You have learned many individual laws and principles by which the chemist works but you have not yet tried to use them together to solve real chemical problems. The principal use which the chemist makes of gas laws, laws of chemical combination and atomic-molecular theories with their symbols and formulas, is in studying the composition of matter and the changes which it undergoes during chemical reactions.

2. Equations. The Law of the Conservation of Mass or Weight and the Law of Definite Proportions are the basis for writing *equations* to represent chemical changes. Since equations represent *chemical changes that actually do take place*, all substances taking part in the reaction must be represented by their correct formulas as determined by the Law of Definite Proportions, and, according to the Law of Conservation of Matter, there can be no gain or loss in the amounts of the elements before, during or after the reaction takes place. This means that *there must be the same number of atoms of each element shown on each side of the equation.* Since each atom is represented by one symbol there must therefore be the same amounts of each symbol on each side of the equation.

Chemical equations represent reactions that actually do take place, and *you cannot write a chemical equation if you do not know what substances take part in the reaction and what substances are formed.* Many students worry about equations and try to memorize them. Do not memorize equations. Learn how to write them correctly and then learn the different reactions

in words. For example, the decomposition of mercuric oxide is written as

$$2\ HgO \longrightarrow 2\ Hg + O_2$$

Instead of learning this as a collection of figures and letters, learn that mercuric oxide decomposes to yield mercury and oxygen. If you know this fact and also know how to write equations you will be able to write the equation as shown above. Remember that *equations must represent actual reactions that do take place.*

3. Balancing equations. The substances entering into the chemical reaction are known as the *reactants* and are represented by formulas on the left-hand side. The substances which are formed by the reaction are known as the *resultants* and are represented by formulas on the right-hand side of the equation. An arrow is placed between the two sides of the equation to indicate "yields", "forms" or "produces". Since the reactants are placed on the left and the resultants on the right the arrow usually points towards the right. You will find that, under particular circumstances, the reaction may go in the reverse direction; this will be shown by an additional arrow placed below the first arrow and pointing towards the left. Since you must know what actually happens before you write the equation, you should have no difficulty in learning how to use the arrows correctly.

The process of retaining the correct formulas in accordance with the Law of Definite Proportions while equalizing the numbers of symbols on each side to agree with the Law of the Conservation of Mass is called *balancing* the equation. To balance an equation:

Step I. Write the *correct formula* of each reactant and resultant with plus signs between each formula and the arrow in its proper place. Until you become more familiar with equations it is a good idea to leave enough space in front of each formula to put in any balancing figures that you may require.

Step II. Starting with the first symbol in the formula of the first reactant, make sure that you have represented among the resultants the *same number of atoms of each element* to agree with the Law of the Conservation of Mass. If you find it necessary to increase the number of atoms of any element it must be done by *multiplying the whole formula* by the appropriate factor placed in front of the formula. Remember that you *cannot alter a formula* since it is fixed by the Law of Definite Proportions.

Step III. If you have found it necessary to multiply a formula, remember that *a number placed before a formula multiplies every symbol in the formula* by that number and you may have disturbed the balance of the other atoms. Go back, adjust the reactants to supply enough atoms, and recheck the symbols and the formulas until you have the correct proportions of each reactant and resultant.

Step IV. As a final check, make sure that you have the same number of atoms of each element on each side of the arrow.

Nothing can take the place of good common sense, understanding and experience in working out the proper proportions in an equation. There are a few pitfalls which might be pointed out before we consider some examples.

(1) Remember to make adjustments only by the numbers that you place *in front* of the formulas, since they multiply the numbers of molecules without changing the composition of any substances.

(2) In most cases the elementary gases are diatomic. Their molecular formulas as substances are, H_2, O_2, N_2, Cl_2, Br_2, F_2. The metals and many non-metals are represented as being monatomic, e.g., Na, K, Ca, Ba, Mg, Fe, Ag, Cu, Pb, Si, C, S, B.

(3) Substances, such as water, which are present in the reaction as solvents or dispersion media, are not usually shown in the equation. Although heat is energy and not matter it is sometimes indicated by the number of calories evolved or absorbed.

(4) A substance acting only as a catalyst is not usually shown in the equation since it does not take part in the chemical change. Sometimes, however, it is indicated by placing it above or below the arrow or on both sides of the equation.

(5) Radicals frequently move as a whole from one substance to another during a reaction, and, after you have some experience in balancing, you may balance them as if they were one symbol. In some cases, however, radicals will decompose and their atoms must be considered separately. CO_3 may give rise to CO_2 and OH to H_2O; in the latter case the additional H atoms are supplied by the other reactants. After you have gained some experience you may find it convenient to leave the H atoms until the last, as you will probably balance them when you balance the others. You should practise balancing equations until you can do it easily as well as correctly.

Let us see how the equations that we used in earlier chapters were balanced.

Example 1. The decomposition of mercuric oxide by heat. The reaction must first be learned *in words*.

Mercuric oxide yields mercury and oxygen.

Step I. Write the correct formulas for reactants and resultants.

$$HgO \longrightarrow Hg + O_2$$

Note that oxygen is expressed by O_2, not by O or 2O.

Step II. Since there are two atoms of oxygen on the right and only one atom on the left, and since the correct formula for oxygen is O_2, we must increase the number of oxygen atoms on the left. This can only be done by multiplying HgO by 2.

$$2\ HgO \longrightarrow Hg + O_2$$

Step III. In balancing the number of oxygen atoms we have now upset the balance of mercury atoms. As we have two mercury atoms on the left we must have two on the right, and we obtain them by multiplying Hg by 2.

$$2\ HgO \longrightarrow 2\ Hg + O_2$$

Step IV. The last step did not affect the oxygen atoms so we can consider the equation balanced. As a final check we find two mercury atoms and two oxygen atoms on the left and the same number of the same atoms on the right. The equation is therefore balanced. Note that we did not alter any of the formulas.

Example 2. The preparation of oxygen from potassium chlorate. We know: Potassium chlorate gives potassium chloride and oxygen.

Step I. Write the correct formulas for reactants and resultants.

$$KClO_3 \longrightarrow KCl + O_2$$

Step II. The potassium and chlorine are already balanced so we go on to the oxygen atoms. We see that there are three on the left and two on the right. Since we are not permitted to change any formulas, the only way to balance 2 against 3 is to turn both of them to their least common multiple, 6. We therefore multiply the $KClO_3$ by 2 and the O_2 by 3.

$$2\ KClO_3 \longrightarrow KCl + 3\ O_2$$

Step III. By multiplying the $KClO_3$ by 2 we have altered the amounts of the potassium and chlorine so that they are now out of balance. We have two atoms of each on the left and only one atom of each on the right. Multiplying the formula KCl by 2 will restore the balance.

$$2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2$$

Step IV. On a final check we find that we have two potassium, two chlorine, and six oxygen atoms on each side of the equation.

It will be noticed that there is no mention of the heat used or the catalyst employed. These are factors affecting the *condition* of the reaction and not the *substances* that take part.

Example 3. The reaction of aluminum with dilute sulphuric acid. First note the fact that this reaction does take place and learn the correct names for the resultants. We know that aluminum sulphate and hydrogen are produced.

Step I. Write the correct formulas.

$$Al + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + H_2$$

Note that hydrogen is expressed as H_2 not 2 H or H.

Step II. There is one aluminum atom on the left and two on the right so the left-hand one will have to be multiplied by 2. There are three sulphate radicals on the right but only one on the left, so the left-hand radical will have to be tripled.

$$2\ Al + 3\ H_2SO_4 \longrightarrow Al_2(SO_4)_3 + H_2$$

Step III. The balancing of the aluminum and sulphate has now unbalanced the hydrogen since there is now six atoms on the left and only two on the right. We must therefore multiply the hydrogen on the right by 3. We then get:

$$2\ Al + 3\ H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3\ H_2$$

Step IV. A final check shows two aluminum, six hydrogen, three sulphur and twelve oxygen atoms on each side, so the equation is balanced. You will note that we balanced the sulphate radical as if it were one single atom since it did not break up during the reaction.

4. Types of chemical change. Equations may be used to represent various types of chemical change.

(1) *Decomposition*, the breaking down of compounds into more simple substances, e.g.,

$$2\ H_2O \longrightarrow 2\ H_2 + O_2$$
$$NH_4Cl \longrightarrow NH_3 + HCl$$

(2) *Double decomposition*, the changing of partners by atoms and radicals. This is sometimes called *metathesis*, e.g.,

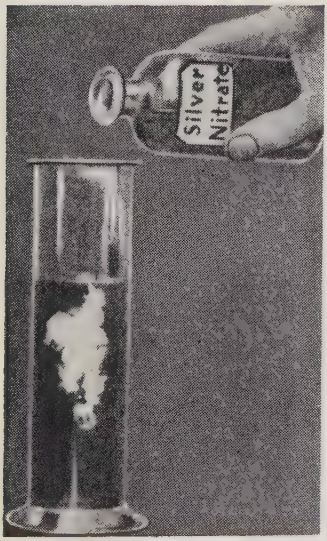
$$KOH + HCl \longrightarrow KCl + H_2O$$
$$KCl + NaNO_3 \longrightarrow KNO_3 + NaCl$$

(3) *Combination*, the formation of more complex compounds, e.g.,

$$2\ Cu + O_2 \longrightarrow 2\ CuO$$
$$NH_3 + HCl \longrightarrow NH_4Cl$$

(4) *Replacement* or *displacement*, the replacement of one element in a compound by another element, e.g.,

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$
$$Fe + CuSO_4 \longrightarrow FeSO_4 + Cu$$



From Black & Conant: "New Practical Chemistry", courtesy of The Macmillan Company.

Fig. 59.

From Bayles & Mills: "Basic Chemistry", courtesy of The Macmillan Company.

Fig. 60.

Fig. 59. Double decomposition occurs when silver nitrate is added to hydrochloric acid to precipitate silver chloride.

Fig. 60. Replacement occurs when a zinc strip is placed in lead nitrate. Lead crystals deposit on the zinc.

5. Calculations from equations. Many calculations may be made from balanced equations if we remember the manifold meaning of symbols and formulas. To do these calculations it is necessary to remember the following:

(*i*) The formula weight is the sum of the atomic weights of *all* the symbols represented by the formula.

(*ii*) The proportions shown in the equation hold down to a few molecules, so that any multiple or sub-multiple of the relative quantities shown in the equation may be considered by taking the *same fraction* of each of the quantities in the balanced equation.

(*iii*) The gas laws may be used to change volumes to and from conditions of standard temperature and pressure (S.T.P.).

(*iv*) The vapour volume of one mol of a substance at S.T.P. is 22.4 litres. Each formula represents a mol or a gram molecular weight; if the substance is a gas or vapour we may substitute the volume at S.T.P. for this weight.

6. Calculations involving weights only. The simplest calculations are those of finding the weights of the reactants or resultants, and it is well to proceed systematically each time, just as in balancing equations.

Step I. Write the balanced equation for the reaction.

Step II. Insert the weights represented by the symbols and find the weights represented by the formulas.

Step III. Note the weight proportions between the substances as shown by the balanced equation. These are equivalent amounts.

Step IV. Take the proper fraction of these equivalent amounts to find the desired quantity.

Example 1. To find the weight of mercuric oxide required to prepare 5 grams of mercury.

Step I. Write the balanced equation for the reaction.

$$2\ HgO \longrightarrow 2\ Hg + O_2$$

Step II. Find the weights represented by the formulas
The equation: $2\ HgO \longrightarrow 2\ Hg + O_2$ shows the symbols.
They mean: 2 mols $\longrightarrow$ 2 gram atoms + 1 mol.
The weights are:
$2 \times (200.6 + 16.0) \longrightarrow 2 \times 200.6 + 32.0$
The equivalent quantities are:

$$433.2 \longrightarrow 401.2 + 32.0$$

Step III. The equation shows *all* the equivalent proportions. 433.2 unit weights of mercuric oxide are equivalent to 401.2 unit weights of mercury and 32 unit weights of oxygen. The common unit of weight in scientific work is the gram, so we may say:

(*i*) 433.2 g. of mercuric oxide corresponds to:
401.2 g. of HgO
32.0 g. of O_2
(*ii*) 401.2 g. of mercury corresponds to 433.2 g. of HgO
32.0 g. of O_2
(*iii*) 32.0 g. of oxygen corresponds to 433.2 g. of HgO
401.2 g. of O_2

For this particular problem we would only need to note that *433.2 g. of mercuric oxide produces 401.2 g. of mercury.* Other problems might require other proportions.

Step IV. The desired quantity may be calculated by taking the proper fraction of the equivalent quantities. In performing the arithmetical work it is a good idea to remember to keep the unknown quantity at the end of the statements in your calculations. In this case the unknown is the mercuric oxide.

401.6 g. of Hg are produced from 433.2 g. of HgO. ∴ 5.0 g. of Hg will be produced from $\frac{433.2 \times 5}{401.2}$ g. of HgO

or, 5.0 g. of Hg are produced from 5.39 g. of HgO.

In a similar manner we might calculate the number of pounds of mercuric oxide required to produce a given number of pounds of mercury. The unit weights represented by the formulas may be pounds, kilograms, tons, hundredweights or any other units of weight. As long as we *use the same units* of quantity the equation can tell us the equivalent proportions of these units. Unit weights are often called *parts* in technical formulations to emphasize that any units may be used. The next three examples will illustrate this point.

Example 2. What are the weight relations in the reaction between aluminum and sulphuric acid?

Step I. Write the balanced equation.

$$2\ Al + 3\ H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3\ H_2$$

Step II. Find the weights represented by the formulas.

(*i*) Symbols: $2\ Al + 3\ H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3\ H_2$

(*ii*) Meaning: 2 gram atoms + 3 mols ⟶ 1 mol + 3 mols.

(*iii*) Weights:

$$2 \times 26.97 + 3\begin{Bmatrix} 2 \times 1.008 \\ 1 \times 32.06 \\ 4 \times 16.00 \end{Bmatrix} \longrightarrow \begin{Bmatrix} 2 \times 26.97 \\ 3 \times 32.06 \\ 12 \times 16.00 \end{Bmatrix} + 6 \times 1.008$$

(1 mol = 98.076) (1 mol = 342.12)

(*iv*) Total weights: 53.94 g. + 294.228 g. ⟶ 342.12 g. + 6.048 g.
(*v*) Check: 348.168 g. ⟶ 348.168 g.

Step III. Note all the proportions.

(*i*) 53.94 g. of Al corresponds to { 294.228 g. of H_2SO_4 / 342.12 g. of $Al_2(SO_4)_3$ / 6.048 g. of H_2

(*ii*) 294.228 g. of H_2SO_4 corresponds to { 53.94 g. of Al / 342.12 g. of $Al_2(SO_4)_3$ / 6.048 g. of H_2

(*iii*) 342.12 g. of $Al_2(SO_4)_3$ corresponds to { 53.94 g. of Al / 294.228 g. of H_2SO_4 / 6.048 g. of H_2

(*iv*) 6.048 g. of H_2 corresponds to { 53.94 g. of Al / 294.228 g. of H_2SO_4 / 342.12 g. of $Al_2(SO_4)_3$

Step IV. The quantity of any substance may be calculated by taking the proper fraction of these corresponding proportions, e.g., 0.13485 g. of Al would produce:

(*i*) $\frac{0.13485 \times 6.048}{53.94}$ or 0.01512 g. of H_2

(*ii*) $\frac{0.13485 \times 342.12}{53.94}$ or 0.8553 g. of $Al_2(SO_4)_3$ and

(*iii*) $\frac{0.13485 \times 294.228}{53.94}$ or 0.7356 g. of H_2SO_4 is required to dissolve it.

Example 3. To find the weight of copper required to make 10 kilograms of cupric oxide.

Step I. Balanced equation: $2\ Cu + O_2 \longrightarrow 2\ CuO$

Step II. Weights represented in the equation.

$$2 \times 63.57 + 2 \times 16.00 \longrightarrow 2\ (63.57 + 16.00)$$
$$127.14 + 32.00 \longrightarrow 159.14$$

Step III. Proportions for calculation. 127.14 parts of copper are required to make 159.14 parts of cupric oxide.

Step IV. Calculation. To make 10,000 g. of cupric oxide we would need $\frac{10{,}000 \times 127.14}{159.14}$ or 7989.2 g. copper.

Approximate calculations and illustrations do not require so many decimal places.

Example 4. The balanced equation shows the quantitative relations between the reactants and the resultants in any units desired. In the reaction between nitric acid and calcium oxide to give calcium nitrate and water we could proceed as follows:

Step I. $CaO + 2\ HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$

Step II. Proportions. By molecular weights to nearest whole numbers. $56 + 126 \longrightarrow 164 + 18$. The units may be pounds, tons, grams, kilograms, etc. in each case. To find how many tons of lime are required to make 41 tons of calcium nitrate we use the ratio in the balanced equation.

Step III. 56 unit weights of CaO $\longrightarrow$ 164 unit weights of $Ca(NO_3)_2$. Thus 164 tons of calcium nitrate require 56 tons of lime.

Step IV. Then 41 tons of calcium nitrate require $\frac{41 \times 56}{164}$ or 14 tons of lime.

7. Calculations with volumes at standard temperature and pressure. If the quantities are expressed in grams it is possible to calculate the *volumes* of the gaseous substances first at S.T.P. and then at any temperature and pressure using 22.4 litres as the gram molecular volume.

Example 1. The use of zinc to prepare hydrogen from sulphuric acid.

Step I. $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

Step II. 65 g. + 98 g. $\longrightarrow$ 161 g. + 2 g. or 22.4 litres at S.T.P.

Note that gram molecular weights are now used so that the conversion factor 22.4 litres per mol may be used to convert weight to volume at S.T.P. A different conversion factor will be used by engineers to convert pounds to cubic feet.

Suppose we wish to use this equation to find how much zinc was required to make 224 ml. of hydrogen at S.T.P. We would proceed as in the weight calculations.

Step III. (proportions) 65 g. of zinc will liberate 22,400 ml. of hydrogen at S.T.P.

Step IV. (calculations) 224 ml of hydrogen are produced by $\frac{224 \times 65}{22{,}400} = 0.65$ g. of zinc.

This is exactly the same procedure as for weight calculations except that *if the substances are gases or vapours we may represent each gram mol as occupying 22.4 litres at S.T.P.*

Example 2. To find the weight of potassium chlorate required to prepare 1 litre of oxygen at S.T.P.

Step I. (equation) $2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2$

Step II. (weights) 245.2 g. $\longrightarrow$ 149.2 g. + 96 g.

(weights and volumes) 245.2 g. $\longrightarrow$ 149.2 g. + 3×22.4 litres.

Step III. When a specific question is asked we note only the essential proportions.

67.2 litres of O_2 at S.T.P. are produced by 245.2 g. of $KClO_3$.

Step IV. To prepare 1 litre of oxygen at S.T.P. we require $\frac{1 \times 245.2}{67.2} = 3.65$ g. of $KClO_3$.

8. Calculations with volumes at any temperature and pressure. By using the gas laws we may calculate from S.T.P. conditions to any temperature and pressure conditions after we have found the volume at S.T.P. from the equation. We may also take a volume at any temperature and pressure and correct it to a volume at S.T.P. (see Chap. 7, sec. 8). We may use the corrected volume in the calculation of proportions from an equation.

Example 1. Find the volume of oxygen, at 27°C. and 710 mm. obtained by decomposing 4.332 g. of mercuric oxide.

Step I. (equation) $\mathbf{2\ HgO \longrightarrow 2\ Hg + O_2}$

Step II. (weights and volumes) 433.2 g. $\longrightarrow$ 401.6 g. + 22.4 litres.

Step III. (proportions) 433.2 g. of HgO $\longrightarrow$ 22.4 litres of O_2.

Step IV. (calculation) $\dfrac{4.332 \times 22.4}{433.2} = 0.224$ litres at S.T.P.

Step V. Correct the volume from S.T.P. to the given conditions.

$\dfrac{0.224 \times 760 \times 300}{710 \times 273} = 0.263$ litres or 263 ml. of oxygen.

Example 2. Find the weight of carbon needed to produce 100 ml. of carbon dioxide if its volume is measured at 22°C. and 570 mm. The reverse of Step V should be performed first because *only volumes at S.T.P. may be used in equations.* $\dfrac{100 \times 273 \times 570}{295 \times 760} = 69.4$ ml. at S.T.P.

Step I. (equation) $\mathbf{C + O_2 \longrightarrow CO_2}$

Step II. (weights and volumes) 12 g. + 22.4 l. $\longrightarrow$ 22.4 l.

Step III. (proportions) 22,400 ml. at S.T.P. needs 12 g. C

Step IV. (calculations) $\dfrac{69.4 \times 12}{22{,}400} = 0.0372$ g. of carbon.

The gas may be collected over water in a gas holder or a pneumatic trough and a correction made for the pressure of the water vapour by Dalton's Law (see Chap. 7 sec. 10).

Example 3. Calculate how much iron is needed to make 100,000 litres of hydrogen measured over water at 17°C. and at 755 mm. Suppose hydrochloric acid is used to dissolve the iron.

Step I. (equation) $\mathbf{Fe + 2\ HCl \longrightarrow FeCl_2 + H_2}$

Step II. (weights) You should try to save time by putting down only the essential proportions for a calculation. In this case we need know only the proportions of iron and hydrogen. We might deduce these from the fact that iron has a valence of 2 under these conditions, and one gram atomic weight of iron will displace two gram atomic weights or one molecular weight of hydrogen. In these simple cases such reasoning will eliminate the first two steps. We will find by either method that 56 g. of iron yield 22.4 litres of hydrogen at S.T.P.

Step III. (proportions) 56 g. Fe $\longrightarrow$ 22.4 litres dry H_2 (S.T.P.).

Since we require the volume of moist hydrogen we can use the fact that the total pressure of 755 mm. is the sum of the pressure of the dry hydrogen and the water vapour pressure. The vapour pressure of water at 17°C. is 14.5 mm., so we may find the net pressure of the hydrogen by subtracting 14.5 from 755.

Step IV. Two methods of comparing the volumes are now available. The calculation is included in each method.

(1) Find the volume of the mol of hydrogen under the conditions named above.

$$\frac{22.4 \times 290 \times 760}{273 \times (755 - 14.5)} = 24.4 \text{ litres at } 17°\text{C. and } 755 \text{ mm. Hg.}$$

$\therefore$ 56 g. of iron will produce 24.4 litres of moist hydrogen. To obtain 100,000 litres we would require

$$\frac{100{,}000 \times 56}{24.4} = 229{,}500 \text{ g. or } 229.5 \text{ kg. of iron.}$$

(2) The volume of the 100,000 litres of moist hydrogen may be reduced to dry hydrogen at S.T.P.

$$\frac{100{,}000 \times 273 \times (755 - 14.5)}{290 \times 760} = 91{,}700 \text{ litres of dry } H_2 \text{ at S.T.P.}$$

To obtain this amount of gas we must use:

$$\frac{91{,}700 \times 56}{22.4} = 229{,}500 \text{ g. or } 229.5 \text{ kg. of iron.}$$

9. A mechanical method for calculation from equations. There is an alternative method of calculation which may be used in Step IV. It makes use of a ratio instead of a fractional part.

Example: How many grams of copper are needed to prepare 2.8 litres of nitric oxide? This question shows how a more complex equation may be used for a calculation.

Step I. (equation) $\mathbf{3\ Cu + 8\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 2\ NO + 4\ H_2O}$

This is called an oxidation-reduction equation.

Step II. Write in the formula weights.

3 (63.57) + 8 (63.008) $\longrightarrow$ 3 (187.57) + 2 (30.00) + 4 (18.016).

190.71 + 504.064 $\longrightarrow$ 562.71 + 60.00 + 72.064,

60.00 g. or 2 mols of nitric oxide occupy 2 $\times$ 22.4 or 44.8 litres at S.T.P.

Step III. (proportions) 190.71 g. of copper give 44.8 litres of nitric oxide at S.T.P.

Step IV. (calculations) Write the unknown and known proportions over the proportions from the equation. Use x for the unknown.

$$\frac{x}{190.71} = \frac{2.8}{44.8}$$

$$x = \frac{2.8 \times 190.71}{44.8} = 11.925 \text{ g.}$$

Question Summary

1. What use does the chemist make of the laws of chemical combination?
2. (*a*) What two laws are the basis of chemical equations?
   (*b*) What must you know before you can write an equation?
3. (*a*) Enumerate the steps in balancing an equation.
   (*b*) Why can you not change a formula in order to balance an equation?
4. Describe with balanced equations the classes of chemical change.
5. What should we try to remember in order to make calculations from equations?
6. Enumerate the steps in making calculations involving weights only.
7. What makes it possible to calculate the volumes of gases from equations?
8. How can you apply the standard conditions of temperature and pressure as given in an equation to the conditions of any problem?
9. Describe a mechanical method for calculating from an equation.

Exercises in balancing equations

1. Balance the following equations:
   (*a*) $HgO \longrightarrow Hg + O_2$
   (*b*) $KNO_3 \longrightarrow KNO_2 + O_2$
   (*c*) $Na_2O_2 + H_2O \longrightarrow NaOH + O_2$
   (*d*) $Al + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + H_2$
   (*e*) $Na + H_2O \longrightarrow NaOH + H_2$
2. Write balanced equations for the following reactions:
   (*a*) Decomposition of water by electrolysis.
   (*b*) Synthesis of water from the elements.
   (*c*) Oxidation of carbon to carbon dioxide.
   (*d*) Burning of sulphur to sulphur dioxide.
   (*e*) Calcination of magnesium.
   (*f*) Dissolving of zinc in hydrochloric acid.
   (*g*) Reduction of cupric oxide by hydrogen.
   (*h*) Preparation of hydrogen peroxide from barium peroxide by sulphuric acid.
   (*i*) Rusting of iron to produce Fe_2O_3.
   (*j*) Hydration of calcium oxide.
   (*k*) Reaction of sulphur dioxide with water.
   (*l*) Reaction of carbon dioxide with water.
   (*m*) Heating of ammonium chloride with slaked lime.
   (*n*) Reaction of ammonia with heated copper.
   (*o*) Action of clean calcium metal on water.
   (*p*) Action of iron in a copper sulphate solution.

3. Write balanced equations for the oxidation of the following elements and write the names of the oxides after the formulas: Al, Ba, Ca, C, Cu, Fe, Pb, Mg, Hg, K, Ag, S, Sn, Zn. (The valences are given in Chap. 10, sec. 6.)

4. Write balanced equations for the reaction of the following metals with: (*a*) hydrochloric acid; (*b*) sulphuric acid; (*c*) silver nitrate. Name the salt that is formed. K, Na, Ba, Mg, Al, Fe, Sn, Zn.

Exercises in calculations from equations.

A. *Weight calculations.*

1. Calculate the weight of the following metals required to make 10 g. of hydrogen from an excess of sulphuric acid: Al, Fe, Mg, Sn, Zn.

2. Calculate the weight of the following substances that would be required to make 1 g. of oxygen: $KClO_3$, Na_2O_2, BaO_2, HgO.

3. Balance the equation for the reaction between NaCl and $AgNO_3$, and calculate the weight of $AgNO_3$ required to prepare 1 kg. of AgCl.

4. Given: $Zn + 2\ NaOH \longrightarrow Na_2ZnO_2 + H_2$. Calculate (a) the weight of NaOH required to react with 5.0 g. of Zn; (b) the weight of Zn required to make 0.100 g. of Na_2ZnO_2.

B. *Weight and volume at S.T.P.*

5. Calculate the volume of oxygen at S.T.P. required to burn 100 g. of each of C, S, P, H and Mg.

6. Calculate the weight of the following metals required to make 1 litre of hydrogen at S.T.P.: Al, Fe, Mg, Sn, Zn.

7. Calculate the volume of H_2S gas at S.T.P. required to precipitate 3.2 g. of copper sulphide from a solution of copper sulphate, according to the equation, $CuSO_4 + H_2S \longrightarrow CuS + H_2SO_4$

8. How many litres of CO_2 at S.T.P. are required to react with 5 g. of $Ca(OH)_2$?

C. *General weight and volume calculations.*

9. How many litres of CO_2 at 27°C. and 700 mm. can be made by heating 4 g. of $CaCO_3$ (limestone)?

10. What volume of oxygen will be produced by the decomposition of 1 g. of $KClO_3$, if the oxygen is collected over water at 30°C. and 740 mm.?

11. If 250 ml. of hydrogen measured at 35°C. and a net pressure of 690 mm. were made by dissolving zinc in excess hydrochloric acid, how much zinc was dissolved?

12. Chlorine can be obtained by heating NaCl, H_2SO_4 and MnO_2. $4\ NaCl + 2\ H_2SO_4 + MnO_2 \longrightarrow MnCl_2 + 2\ Na_2SO_4 + Cl_2 + 2\ H_2O$.

(*a*) What volume of chlorine at 52°C. and 10 atmospheres pressure can be made from 500 kg. of sodium chloride?

(*b*) What weight of MnO_2 is required for this amount of NaCl?

See also **Problems** at end of chapters.

Chapter **13**

Carbon and Its Oxides

CARBON

1. Introduction. Carbon is found in the earth's crust both in the free state and in combination with other elements. While it represents only a small percentage of the crust of the earth, it is an element of great importance since it forms a part of all living things. In this chapter we shall consider carbon, carbon monoxide and carbon dioxide. There are many thousands of organic compounds containing carbon, but we shall discuss them in Topic Eight.

Carbon is one of the elements which exhibit the property of allotropy and it is found on the earth in several forms, two of which are crystalline and several are amorphous. A *crystalline* substance is one which possesses a geometric form and an *amorphous* substance is one which does not have any definite shape.

2. The crystalline forms of carbon.

(1) *Diamond.* Diamonds have been known to man for many years and they have been greatly prized for their beauty, and, since they are scarce, for their value. India, Brazil and South Africa have been the source of many of the famous diamonds. They are found in rocky masses, which are probably the necks of ancient volcanoes, and they were no doubt produced by the crystallization of carbon under great pressures. In 1893 Moissan produced very small diamonds by dissolving carbon in melted iron in an electric furnace and pouring the resulting mass into water. The con-

traction of the iron on solidifying produced very great pressures which caused the formation of the small diamonds. These diamonds are too small to be of any value and this method cannot compete with the mining of the natural stones.

The specific gravity of diamond is 3.5 and it is the hardest substance known. Its beauty depends upon its high refractive index, which enables it to reflect a large amount of the light which falls upon it. Rough diamonds are not very lustrous and the stone is cut so as to produce facets to aid in the reflection of light. Stones not suitable for jewellery are used for the teeth of stone-saws and as drills for rock. The diamond burns in air at about 900°C. to form carbon dioxide but it is not chemically active.

(2) *Graphite.* The other crystalline form of carbon is known as *Graphite.* Because of its appearance it was once thought to be a compound of lead and was called *plumbago.* It is found in Ceylon, Korea and Siberia, and smaller deposits are found in other countries, including the United States and Canada. Carbon vaporizes at a temperature of about 3500°C. in the absence of air and the vapour forms crystals of graphite upon cooling. The commercial production of graphite depends upon this principle. Coke or hard coal is heated in an electric furnace with a core of granulated carbon, and the carbon in the coal is converted into graphite.

Graphite has a specific gravity of 2.2. It is very soft and will leave a mark when rubbed upon paper. Like diamond it is very inert but it will burn in oxygen. Because of its chemical inertness it is used to make crucibles which must be exposed to high temperatures. It is also used as a lubricant for which purpose it may be used alone or as a suspension in oil or water. The "lead" of a pencil is composed of graphite mixed with clay and waxes and the "hardness" of the pencil depends upon the proportions in which the constituents are mixed, soft leads containing less clay.

3. Amorphous forms of carbon. Amorphous carbon is found in several forms, such as coal, coke, charcoal, bone-black and lampblack. These forms are distinguished from one another by their carbon content and their structure.

(1) *Coal.* As you know, coal is mined in the earth, where it has been formed from decayed vegetation during many years of high pressures and high temperatures. During the ages the wood has been changed so that very little material other than carbon is left, and the different types of coal are due to the extent to which this conversion has taken place. *Peat* contains about 50 per cent volatile matter and about 25 per cent of fixed carbon. It is found in bogs from which it is cut and then dried. *Lignite* or *brown coal*, found in Canada mainly in Saskatchewan, contains about 30 per cent of volatile matter and about 30 per cent of fixed carbon. Further geologic changes have led to *bituminous* or *soft* coal containing about 35 per cent of volatile matter and about 50 per cent of fixed carbon. It is found mainly in Alberta, Nova Scotia, New Brunswick and British Columbia. The final stage is *anthracite* or *hard coal*, which contains about 3 per cent of volatile matter and about 85 per cent of fixed carbon. All forms of coal contain small amounts of mineral matter or ash.

(2) *Coke.* Coke is prepared by heating soft coal in retorts in the absence of air. A gas known as *coal gas* is given off and coke remains. Coal gas consists of a mixture of several gases, the larger quantities of which are carbon monoxide and hydrogen. Coal gas is used for heating in houses, industrial plants and laboratories, and is prepared by the method illustrated in the diagram in Fig. 61.

The soft coal is placed in an iron retort which is heated by a coal, gas, or oil fire, and the gas driven off. The gas is led to the *hydraulic main* where tar is condensed. The gas then goes to the *condenser* where it is forced through water seals by means of baffles. A further condensation of tar takes place in the condenser and the gas passes to the *scrubbers*. The scrubbers are tall towers filled with loosely-packed coke, or similar material,

through which the gas passes upward. In the first scrubber the coke is sprayed with water which dissolves ammonia and some of the hydrogen sulphide which is present. The second scrubber removes benzene and toluene which are dissolved in the oil which is sprayed over the coke. The gas is then passed through the purifier which contains moist ferric oxide or quicklime; this removes the balance of the hydrogen sulphide. It is then passed into the gas holder. The coke is almost pure carbon and has a porous structure. It is used in the blast furnace for the reduction of iron ore and it is also used as a fuel.

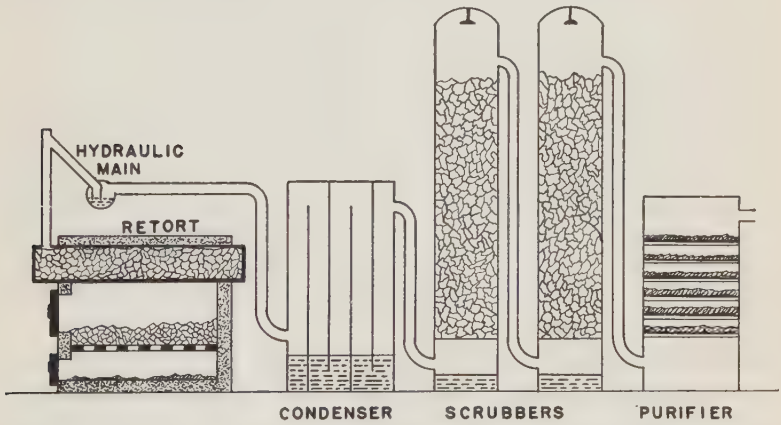


Fig. 61. Diagram of a plant for producing coal gas and its by-products.

(3) *Charcoal.* Charcoal is prepared by heating wood in the absence of air. The volatile portions of the wood pass off through pipes and are condensed to a liquid. This liquid is known as *pyroligneous acid*, and from it are obtained methyl alcohol, acetone and acetic acid. The charcoal remains in the retort.

Charcoal is very porous and thus presents a large surface. It is a good adsorber of gases and is used in gas masks, for which purpose it is made usually from cocoanut shells. It is used as a clarifying and decolorizing agent in the refining of sugar and other products.

(4) *Boneblack.* Boneblack or *animal charcoal* is prepared by the destructive distillation of bones and other animal refuse. Since bones consist of about 40 per cent mineral

matter, boneblack does not contain much carbon. It is a good adsorber and is used as a decolorizer in the refining of sugar. The presence of the mineral matter aids in the dispersion of the carbon particles and produces a large surface for adsorption.

(5) *Lampblack and carbon black.* Finely divided amorphous carbon is produced by burning natural gas, acetylene, tar, or oils in a limited supply of air. The carbon obtained from natural gas is known as *carbon black* and that from acetylene, *acetylene black.* That obtained from other materials is known as *lampblack.* In preparing it from natural gas the flame is allowed to play against a revolving drum from which the resulting coating is scraped. Carbon black is used as a black pigment in printer's ink, stove and shoe polish, and as a filler in the manufacture of automobile tires. Acetylene black makes rubber a conductor of electricity.

(6) *Gas Carbon.* In the preparation of coal gas, some of the hydrocarbons of the gas are decomposed by the high temperature and the carbon is deposited on the walls of the retort. This form of carbon is harder and more crystalline than some of the other varieties. Since it conducts electricity fairly well it is used in manufacturing carbon rods for use as electrodes.

4. Properties of carbon.

A. *Physical properties.* Carbon is odourless and tasteless. It is insoluble in most solvents but it dissolves slightly in some molten metals. It is present in the products of the blast furnace, and the properties of iron and steel depend upon the percentage of carbon that is present. Carbon does not melt, but passes into a vapour at about 3500°C. When heated to a high temperature it becomes incandescent. The filaments in electric lamps were formerly made of carbon but they are now made of tungsten, which is much stronger, has less resistance and is more efficient in producing light.

B. *Chemical properties.* Carbon combines with other elements very slowly at ordinary temperatures. At high temperatures it combines with some metals to form *carbides* such as those of calcium, CaC_2 and iron, Fe_3C. When carbon burns freely in air it produces carbon dioxide, but when burned with a limited supply of air it forms carbon monoxide.

$$C + O_2 \longrightarrow CO_2$$
$$2\ C + O_2 \longrightarrow 2\ CO$$

Carbon unites with sulphur to form *carbon disulphide*, CS_2, with silicon to form *silicon carbide*, SiC, and with hydrogen to form the *hydrocarbons*. This latter reaction is very interesting because it is the means of converting coal into oil.

CARBON MONOXIDE

5. Introduction. Carbon monoxide is one of the two oxides of carbon, and it is produced when substances containing carbon are burned in a limited supply of air. You are no doubt familiar with the dangers of poisoning from this gas and everyone should be fully aware of the possibility of its production by accidental means.

6. Preparation of carbon monoxide.

A. *Laboratory methods.* Carbon monoxide may be made in the laboratory by heating formic acid in the presence of sulphuric acid. This process consists of the removal of a molecule of water from a molecule of the formic acid and the sulphuric acid aids in the removal of the water. The gas may be collected by means of a pneumatic trough.

$$HCOOH \longrightarrow H_2O + CO$$

Oxalic acid may be used instead of formic acid in the preparation of carbon monoxide. In this case a molecule of carbon dioxide is obtained at the same time. The carbon dioxide may be removed by passing the mixture of gases

through a solution of sodium hydroxide. The carbon dioxide reacts to form sodium carbonate and the carbon monoxide passes through unchanged.

$$\begin{matrix}\text{COOH}\\ |\\ \text{COOH}\end{matrix} \longrightarrow H_2O + CO_2 + CO$$

B. *Industrial methods.* (1) *From water gas.* You have learned that water gas may be made by passing steam through white-hot coke (see Chap. 6, sec. 4). The method of producing water gas is shown in Fig. 62.

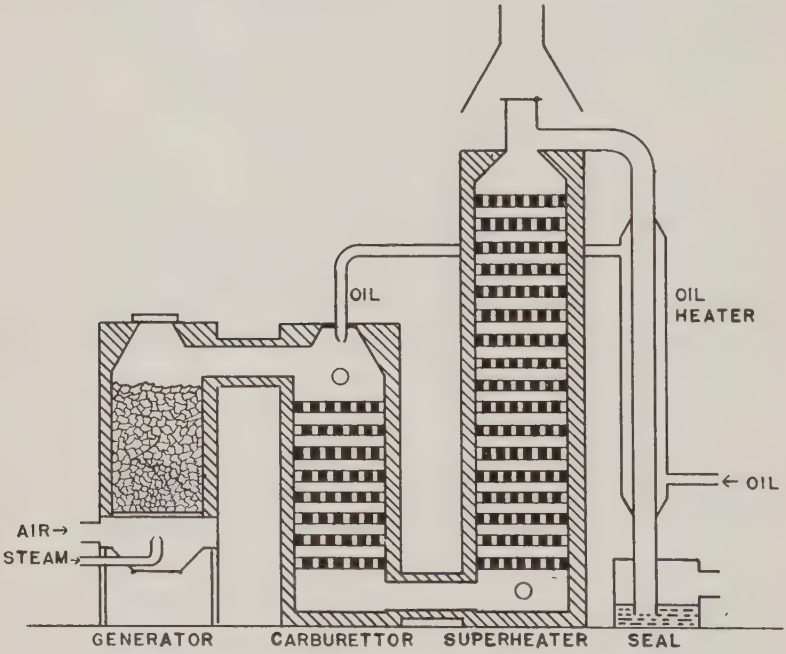


Fig. 62. Diagram of a plant for producing water gas.

The generator is filled with anthracite coal or coke which is brought to incandescence by a blast of air which enters from the bottom. The gas produced in the generator is largely a mixture of carbon monoxide and nitrogen and is passed to the carburettor which is a tower filled with a checker-work of fire-brick. A blast of air enters the top of the carburettor and the gas from the generator is partly burned. The heat from this

combustion brings the checker-work to a white heat and the partially burned gas passes into the superheater, which is a tower filled with more checker-work. At the bottom of the superheater another blast of air completes the combustion of the gas and raises the temperature of the checker-work until it is a bright red. From the top of the superheater the gases escape into the open air for about 8 minutes while *air* is blown through the generator and a temperature of about 1100°C. is reached. Superheated steam is now introduced into the generator in place of the air, and the following reactions take place:

$$C + 2\,H_2O \longrightarrow 2\,H_2 + CO_2$$
$$C + CO_2 \longrightarrow 2\,CO$$

The water gas, which is the mixture of carbon monoxide and hydrogen, is passed through the carburettor while a small stream of heated oil is introduced at the top. The oil is decomposed or cracked into smaller molecules by the hot checker-work to form illuminating gases which mix with the water gas and increase its heating value. The gases then pass through the superheater where the larger molecules are converted to non-condensable gases. The gases from the superheater are led to a purifier through a jacketed tube which heats the oil used in the carburettor. The steam blast is kept on for about 6 minutes, at which time the temperature of the checker-work has dropped below that at which the decomposition of the oil takes place. The steam is then shut off and the air blast resumed. Most coal gas plants have a water gas plant as well as the gas retorts in order to build up their gas supply quickly, because it takes less time to put a water gas plant into operation than to heat a coal gas retort. Water gas plants in operation may be recognized by the intermittent flame which escapes from the superheater. Water gas not enriched by oil burns with an almost colourless flame but the gases added by the carburettor provide a visible flame.

(2) *From blast furnace gas.* The gas escaping from the top of a blast furnace contains large quantities of carbon monoxide, some nitrogen, a little hydrogen and some other gases. This gas is known as *blast furnace gas*, and is used as a low-grade but cheap fuel.

(3) *From producer gas.* If a blast of air and steam is passed through hot coal, wood or some other materials, *producer gas* is obtained. The method of preparing this gas is shown in the diagram in Fig. 63.

The generator consists of a vertical cylinder lined with fire-brick and fitted with a revolving grate, on which is placed a deep bed of ashes. Coal is placed on top of the ashes. A blast of air is sent through the hot coal

which is soon raised to incandescence. Steam is then introduced *into the air blast* and water gas is produced which mixes with the other gases. The amounts of steam and air are regulated carefully so that the temperature of the coal will remain high enough to produce some water gas. A regenerative heating system is used to raise the temperature of the incoming air, but this is not shown in the diagram. As the coal is consumed the amount of ash increases and the circular grate is rotated so the surplus ashes are spilled out and may be removed.

Producer gas contains large quantities of nitrogen, some hydrogen, hydrocarbons, carbon dioxide and about 25 per cent of carbon monoxide. The gas does not have a very high calorific value but it can be used in gas engines and is a low-grade cheap fuel. Producer gas is used instead of burning the coal directly as it offers the convenience of a gaseous fuel. It may be produced from inferior grades of coal.

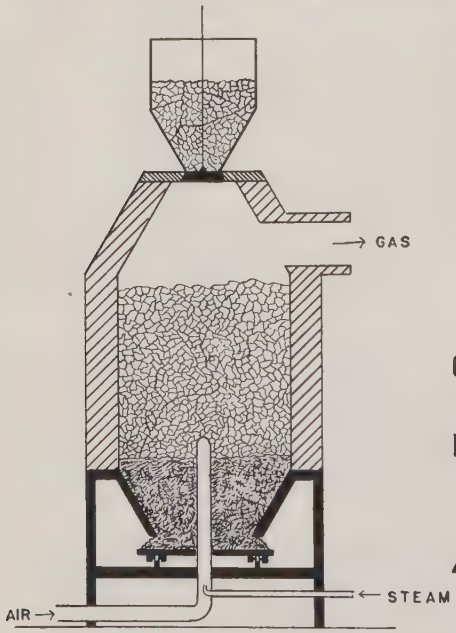


Fig. 63. Producer gas generator.

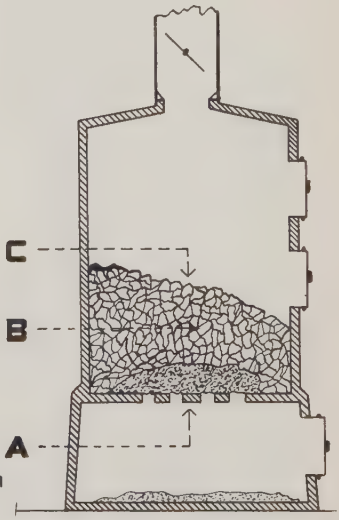


Fig. 64. Coal-burning stove.

7. Properties of carbon monoxide.

A. *Physical properties.* Carbon monoxide is a colourless,

odourless and tasteless gas. It is slightly soluble in water and is just a bit lighter than air. It may be liquefied at $-192°C.$ under a pressure of two atmospheres.

B. *Chemical properties.* Carbon monoxide combines with oxygen to form carbon dioxide. It burns with a blue flame which may be seen flickering above a bed of red-hot coal.

$$2\ CO + O_2 \longrightarrow 2\ CO_2$$

This tendency to combine with oxygen makes it useful as a reducing agent. It combines with some metals to form *carbonyls*, which are unstable poisonous volatile compounds. It combines with chlorine to form *carbonyl chloride*, or *phosgene*, $COCl_2$.

8. Uses of carbon monoxide. Carbon monoxide is used extensively as a fuel in the form of the various gases which have been described. It is used as a reducing agent and the principal reducing action in the blast furnace may be represented by the equation:

$$Fe_2O_3 + 3\ CO \longrightarrow 3\ CO_2 + 2\ Fe$$

It is used in the purification of nickel by the preparation and subsequent decomposition of *nickel carbonyl*, $Ni(CO)_4$. It is also used in the preparation of phosgene. Phosgene is used in the manufacture of dyes and various drugs. It was used as a poison gas in World War I.

9. Carbon monoxide poisoning. The red colouring matter of the blood is a compound called *haemoglobin*, which combines with oxygen in the lungs to form the bright scarlet substance, *oxy-haemoglobin*. Carbon monoxide forms a compound with the haemoglobin which is relatively stable, and the formation of this substance prevents the haemoglobin from performing its function, with the result that the body cannot receive its supply of oxygen and death ensues. Since

carbon monoxide has no taste or odour, its presence cannot be detected by the body. The first symptom is sleepiness which may be ascribed to natural fatigue, and because of a loss of motor activity, the victim may not be able to escape even if he should become aware of his danger. Air containing 1 part of carbon monoxide in 600-700 parts is dangerous.

10. The production of carbon monoxide in combustion. The production of carbon monoxide in the combustion of coal in an ordinary stove or furnace is illustrated in Fig. 64. The coal is burned on the grates with air which enters from below and carbon dioxide is produced.

$$C + O_2 \longrightarrow CO_2 \text{ (at A in Fig. 64).}$$

The heat of this reaction raises the surrounding coal to a high temperature, and as the carbon dioxide passes through the bank of hot coal it is reduced to carbon monoxide.

$$2\ C + CO_2 \longrightarrow 2\ CO \text{ (at B in Fig. 64).}$$

This carbon monoxide is burned to carbon dioxide by means of air which enters above the bed of coal; the gases produced pass up the flue.

$$2\ CO + O_2 \longrightarrow 2\ CO_2 \text{ (at C in Fig. 64).}$$

This reaction is responsible for the flickering blue flame which is frequently seen on the top of a coal fire. If the carbon monoxide is burned completely to carbon dioxide there is no danger. If this final reaction is prevented by a shortage of air above the fire, or when the fire is banked, the carbon monoxide may not be burned and may pass up the flue, thus causing the loss of some valuable heat which would have been available from the combustion of the gas. Besides losing the heat of this reaction, there is a danger that this carbon monoxide may escape into the surrounding air by a block in the flue and leaks in the furnace.

CARBON DIOXIDE

11. Introduction. Van Helmont prepared carbon dioxide by the action of acids on carbonates and learned a great deal about the properties of the gas. He found that it was formed during the combustion of charcoal and during the decay and fermentation of organic matter, as well as being present in mineral waters. He also found that it would extinguish a flame and it would suffocate animals, but he confused it with other gases which will not support combustion. Because he could not generate it in corked bottles without smashing them he called it the wild untamable gas, "gas sylvestre", to distinguish it from ordinary air. In 1755 Joseph Black proved that the gas was a constituent of carbonated alkalies, and since it appeared to be fixed in the solid material, called it "fixed air". Lavoisier showed that it was an oxide of carbon.

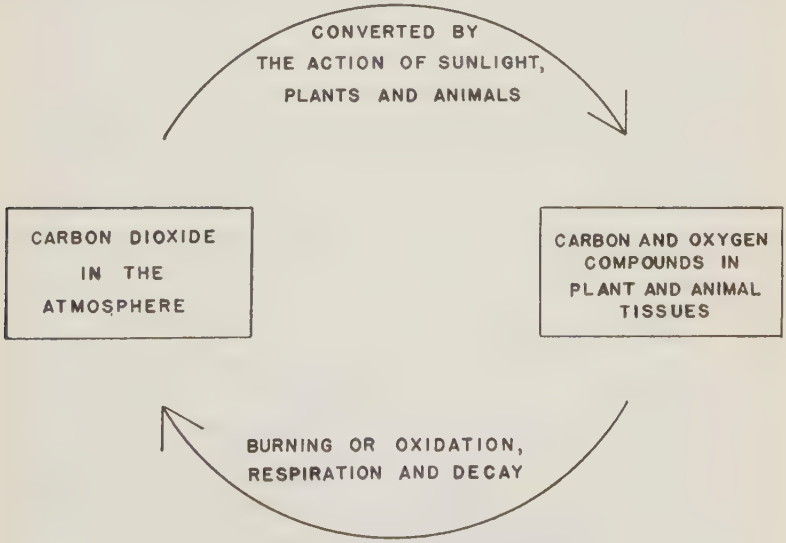


Fig. 65. The carbon cycle in nature.

12. Occurrence. Carbon dioxide is found in the atmosphere to the extent of about 0.03 per cent by volume. It

is produced by the exhalation of all animals and by the complete combustion of substances containing carbon. The amount present in the atmosphere remains constant because all green vegetation removes the gas to convert it into starches, sugars and other plant materials. Some carbon dioxide is removed from the atmosphere by solution in surface water and rain water. The transformations of carbon dioxide in nature constitute the *carbon cycle* which is shown in Fig. 65.

13. Preparation of carbon dioxide.

A. Laboratory method. The common laboratory method of preparing carbon dioxide is by allowing dilute hydrochloric acid to act upon pieces of limestone, chalk or marble. While these substances are most commonly used for this purpose, the action of almost any acid on any carbonate will produce the gas. The apparatus consists of a flask fitted with a stopper carrying a thistle tube and a delivery tube. A pneumatic trough is not usually used. As the gas is heavier than air the delivery tube leads to the bottom of the collecting jar which fills with the gas just as a pail is filled with water from a tap. This method of collecting a gas is known as the upward displacement of air. The apparatus is set up as shown in Fig. 66. Chalk, marble and limestone are all forms of calcium carbonate, so the equation for the reaction is:

$$CaCO_3 + 2\ HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

To determine when the collecting jars are filled, a lighted splinter is held to the mouth of the jar. When the jar is filled the flame of the splinter will be extinguished. This is not a test for carbon dioxide but is only to determine when the jar is filled with the gas.

B. Industrial methods.

(1) *By heating limestone in a kiln.* Carbon dioxide can be obtained by heating limestone in a kiln. The limestone,

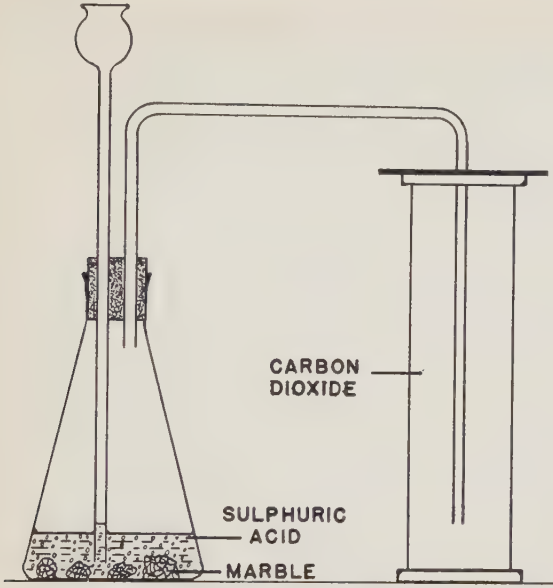


Fig. 66. Preparation of carbon dioxide.

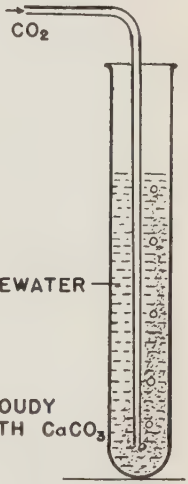


Fig. 67. Test for CO_2.

which is calcium carbonate, is decomposed at about 900°C. into calcium oxide and carbon dioxide. The gas is driven off and the oxide, which is known as *quicklime*, remains.

$$CaCO_3 \longrightarrow CaO + CO_2$$

(2) *As a by-product in fermentation.* Carbon dioxide is obtained as a by-product in the fermentation of sugars. When yeast acts upon certain sugars, alcohol is produced and carbon dioxide is given off (see Chap. 44, sec. 4). As large quantities of industrial alcohol are produced by fermentation, a considerable amount of carbon dioxide is obtained by this method of production.

(3) *By the combustion of fuels.* Carbon dioxide is given off by the complete combustion of substances containing carbon and is thus produced as a by-product in many industrial operations, particularly in burning coke to heat steam boilers. The gas is not pure since it is accompanied by many other

gases and suspended solids; these must be removed before it is used to make "dry" ice or liquid carbon dioxide. It can be obtained more cheaply and in a purer state as a by-product from the heating of limestone and by fermentation where these processes are in use.

14. Properties of carbon dioxide.

A. *Physical properties.* Carbon dioxide is a colourless and odourless gas with an acid taste. It is soluble in water and is heavier than air. At 20°C. it may be liquefied by a pressure of about 56 atmospheres. The carbon dioxide in the commercial cylinders is in a liquid state, and if the cylinder is inverted so that the liquid will come out when the valve is opened, the cooling produced by the sudden evaporation of the liquid will cause the carbon dioxide to freeze to a white solid known as carbon dioxide snow or "dry" ice. Solid carbon dioxide is used in laboratories to produce low temperatures by placing it in liquids with very low freezing points. If it is placed in ether the resulting mixture has a temperature of −79°C.

B. *Chemical properties.* Carbon dioxide is relatively stable. Although it contains a large amount of oxygen, it cannot be used as an oxidizing agent. It may be reduced by some of the more active metals, as sodium and magnesium, but the common reducing agent for it is carbon at high temperatures.

When carbon dioxide is bubbled through solutions of hydroxides, carbonates are formed.

$$CO_2 + 2\ NaOH \longrightarrow Na_2CO_3 + H_2O$$

In the case of calcium or barium hydroxide, the carbonate which is formed is insoluble and a precipitate is produced. This reaction is used as a test for the gas, in which case a solution of calcium hydroxide, known as *limewater*, is used. The gas is either bubbled through the solution or some of

the limewater is shaken in a vessel containing the gas. The limewater turns milky when calcium carbonate precipitates out.

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$

15. Carbonic acid. If carbon dioxide is passed into water some of the gas will dissolve and the resulting solution will act as an acid when tested with litmus paper. This acid gives salts known as *carbonates* and *bicarbonates*. The acid itself is known as *carbonic acid* and is too unstable to be separated from the solution.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

Carbonic acid is only available in dilute solution obtained when carbon dioxide is dissolved in water.

16. Uses of carbon dioxide. Carbon dioxide is used extensively in the production of soda water. At atmospheric pressure about one volume of the gas will dissolve in one volume of water but at an increased pressure the solubility is increased, according to Henry's law (see Chap. 7, sec. 11). When the cap of a bottle of soda water is removed the pressure is decreased and the gas comes out of solution, thus causing the familiar effervescence.

Carbon dioxide is used to extinguish fires. Fires may be extinguished in two ways: first by shutting off the supply of oxygen, and secondly, by reducing the temperature of the burning substances to a point below the kindling temperature. If a fire is covered with an atmosphere of carbon dioxide it will be extinguished through lack of oxygen, which is driven away by the gas as it enters all the crevices in the pile of burning materials. Carbon dioxide is usually applied as a fire extinguisher in the form of a solution in water. The construction of the familiar soda-acid fire extinguisher is shown in Fig. 68.

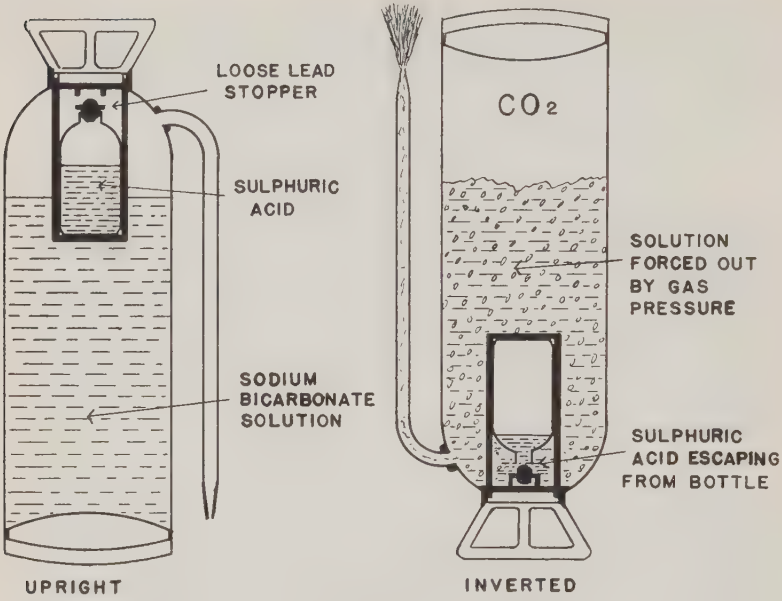
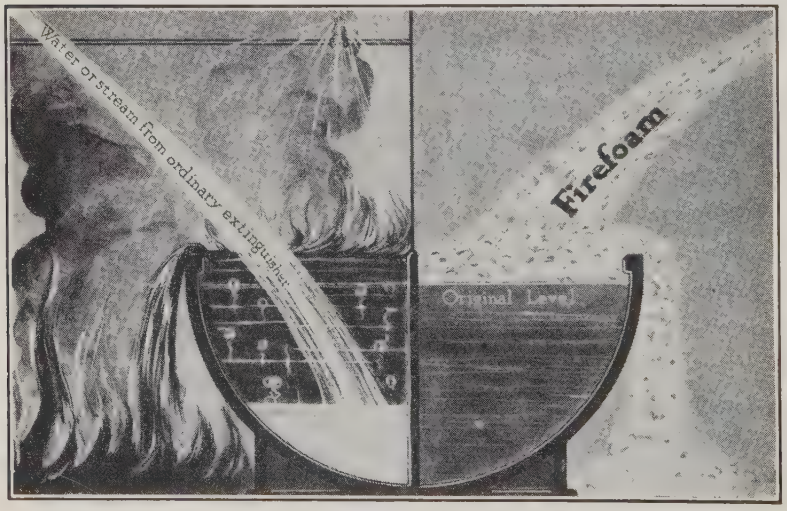


Fig. 68. The action of a soda-acid fire extinguisher.



From Black & Conant: "New Practical Chemistry", courtesy of The Macmillan Company.

Fig. 69. Carbon dioxide foam makes a blanket to smother the fire.

The main portion of the extinguisher is filled with a solution of sodium bicarbonate, while the small bottle is filled with sulphuric acid and closed with a loosely fitted lead stopper. When the extinguisher is inverted the stopper falls out and the acid escapes from the bottle into the solution. Carbon dioxide is produced by the reaction which takes place immediately.

$$2\ NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ H_2O + CO_2$$

The space above the liquid becomes filled with gas whose pressure forces the liquid out of the nozzle with considerable force. When the solution falls upon the burning material the liquid lowers the temperature, while the gas liberated from the solution acts like a blanket in shutting off the oxygen. The solution is therefore more efficient as a fire extinguisher than water alone.

Dense liquids, water, or aqueous solutions should not be used to extinguish oil fires, as the burning oil will float on the liquid and be spread around a greater area. For extinguishing oil fires a blanket of carbon dioxide or a foam is used (see Fig. 69).

Carbon dioxide acts as a stimulant to the body in respiration, and for that reason small quantities of it are added to the oxygen used to relieve cases of asphyxiation.

Solid carbon dioxide is packed into moulds and used as a refrigerant known as *dry ice*, which you have probably seen placed in packages of ice cream. This solid does not form a liquid as ice does when it melts but passes directly to the gaseous form. Small pieces of dry ice may be picked up and held in the fingers momentarily, since a thin layer of gas forms immediately and insulates the skin from the solid itself. If the piece is forced against the skin this insulating layer will be broken and a severe frostbite may result.

Question Summary

1. (*a*) Why is carbon considered to be an important element?

2. (*a*) What are the properties of diamond? Name some of the uses of diamonds which depend on these properties.

(*b*) How may artificial diamonds be prepared?

(*c*) Name the properties of graphite which distinguish it from other crystalline forms of carbon.

(*d*) Give the uses of graphite. Explain the reason for the name "lead" pencil.

3. (*a*) How was coal produced in nature?

(*b*) Name the different types of coal with their approximate carbon content.

(*c*) How is coke prepared? For what is it used?

(*d*) How is coal gas prepared?

(*e*) How is charcoal prepared? What are its uses?

(*f*) What is meant by "adsorption"?

(*g*) How is boneblack prepared? What are its uses?

(*h*) How is lampblack prepared? What are its uses?

(*i*) How is gas carbon prepared? What are its uses?

4. (*a*) Name the physical properties of carbon.

(*b*) Name some of the compounds formed by the combination of carbon with metals and non-metals.

5. Why should the properties of carbon monoxide be well known?

6. (*a*) Describe a laboratory method of preparing carbon monoxide. Write the equation for the reaction.

(*b*) Describe the production of water gas.

(*c*) What is meant by blast furnace gas?

(*d*) Describe the production of producer gas.

7. (*a*) Give the physical properties of carbon monoxide.

(*b*) Describe the combination of carbon monoxide with metals, oxygen and some other elements.

8. Give some of the uses of carbon monoxide.

9. Describe the effect of carbon monoxide on the human body. Why is it a dangerous substance?

10. (*a*) Write the equations for the reactions taking place during the operation of a coal furnace.

(*b*) How may a coal furnace become dangerous?

(*c*) Discuss the presence of carbon monoxide in the operation of gas engines and gas burners.

11. Give a short account of the history of carbon dioxide.

12. Give an account of the carbon cycle in nature.

13. (*a*) Describe the laboratory method of preparing carbon dioxide.

(*b*) Describe the industrial methods of obtaining carbon dioxide.

14. (*a*) Give the physical properties of carbon dioxide.

(*b*) Describe the test for carbon dioxide. Write the equation.

15. Describe the production of carbonic acid. Write the equation. What are the salts of this acid?

16. (*a*) Explain the process involved in the extinguishing of fires? Why is a solution of carbon dioxide in water effective in such a process?

(*b*) Describe the action of a soda-acid fire extinguisher. Write the equation for the reaction.

(*c*) Give some other uses for carbon dioxide.

Problems

1. Assuming that it is pure carbon, how many grams of coke will be required to produce 132 grams of carbon dioxide?

2. How many grams of carbon monoxide will be obtained from 100 grams of formic acid?

3. How many grams of carbon dioxide will be obtained from 500 grams of limestone which is 90% pure?

4. What volume of carbon monoxide at S.T.P. will be obtained by the reduction of 800 ml. of carbon dioxide?

5. What volume of carbon dioxide at S.T.P. will be obtained by the action of 250 grams of hydrochloric acid upon one kilogram of marble?

Chapter **14**

Sulphur, Sulphur Dioxide and Hydrogen Sulphide

SULPHUR

1. Introduction. Sulphur is one of the elements which was known to the ancients. It was used in medicine and as a fumigant as far back as 1000 B.C. It played an important part in the early ideas about the constitution of matter and was used commonly by the alchemists. It was called *brimstone* or *burning stone* and is mentioned by that name in biblical writing.

2. Occurrence. Sulphur occurs in the free state in Sicily, Japan, Spain, Iceland and Mexico, and there are large underground deposits in Texas and Louisiana in the United States. It is found widely in the combined state: as sulphates, the most important being *gypsum*, $CaSO_4.2H_2O$ and *barite*, $BaSO_4$; as sulphides such as *galena*, PbS, *cinnabar*, HgS, *zinc blende*, ZnS and *iron pyrites*, FeS_2; and as ores of silver, copper and other metals. It is found in small amounts in some animal proteins such as egg albumin.

3. Production. Most of the world's supply was formerly obtained from Sicily. The sulphur, together with the rocky material mined with it, is heated in iron retorts and the vapour condensed in large brick chambers, as shown in the diagram in Fig. 70. At first the vapour condenses in the form of a powder, *flowers of sulphur*, on the walls of the chamber, but as the temperature of the chamber wall rises the sulphur melts and is run into moulds where it appears as the *roll sulphur* of commerce.

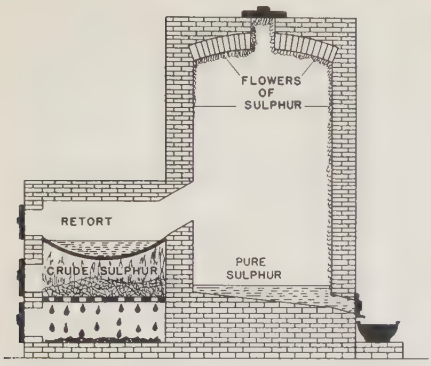


Fig. 70.

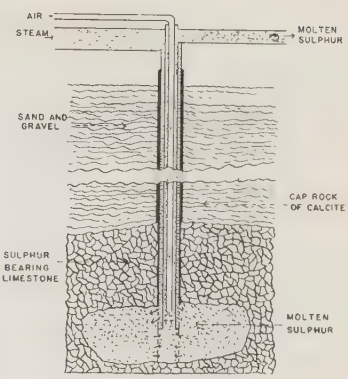


Fig. 71.

Fig. 70. Extraction and purification of sulphur by distillation.
Fig. 71. Frasch process well.

About 80 per cent of the world's sulphur is now obtained from the deposits in Texas. These deposits are covered with a quicksand, which renders ordinary methods of mining impossible. A method of obtaining this sulphur was devised by Frasch in 1900. This is shown in Fig. 71. Three concentric pipes with diameters of 1, 3 and 6 inches are driven down into the deposit. Water which has been heated to 170°C. under pressure is forced into the deposit through the largest pipe. The sulphur will melt and mix with the water. Compressed air is forced down through the smallest pipe. A frothy mixture of air, sulphur and water is produced and this is forced to the surface through the middle pipe. The mixture is run into large bins where the sulphur solidifies and the water drains away. The large piles of sulphur are blasted into smaller pieces and shipped. The Frasch process depends on continuous operation, otherwise the sulphur would solidify in the pipes and could not be brought to the surface. The sulphur obtained from these deposits is about 99 per cent pure.

4. Physical properties of sulphur. Sulphur exists in three allotropic forms, two of which are crystalline and one

is amorphous. The transition temperature at which the change from one crystalline form to another occurs is about 96°C. Below this temperature sulphur forms crystals which are shaped like two pyramids joined together at their bases and is known as *rhombic sulphur*. Above this temperature sulphur crystallizes in long needles which are known as *monoclinic sulphur*.

Rhombic sulphur is a lemon-yellow solid with a specific gravity of 2.1 and a melting point of 114.5°C. It is insoluble in water but it may be dissolved in carbon disulphide and some organic liquids.

Monoclinic sulphur is a little darker in colour than the rhombic form. It has a specific gravity of 1.96 and melts at 119°C. It is soluble in carbon disulphide. If allowed to stand for a few days monoclinic sulphur will change to the rhombic form, since at room temperature it is below the transition temperature of 96°C.

When sulphur is heated in a test tube it melts at 114.5°C. to form a light yellow freely-flowing liquid. On further heating the liquid becomes darker and more viscous, until at about 220°C. the tube can be inverted without the sulphur flowing out. Above this temperature the sulphur becomes a thin liquid which boils at 445°C., producing a yellow vapour.

If liquid sulphur which has been heated almost to the boiling point be cooled suddenly by being poured into water, it forms an amorphous plastic solid, known as *amorphous sulphur*. This form is amber in colour, with varying specific gravity, and has an indefinite melting point. It changes to rhombic sulphur if it is allowed to stand for a few days.

5. Chemical properties. Sulphur burns in air with a purple flame forming sulphur dioxide, SO_2. It burns more vigorously in pure oxygen.

$$S + O_2 \longrightarrow SO_2$$

Sulphur combines with most of the metals to form *sulphides*. In some cases, as with finely divided iron, zinc and copper, the action is so vigorous as to produce incandescence.

$$Fe + S \longrightarrow FeS$$
$$2\ Cu + S \longrightarrow Cu_2S$$
$$Zn + S \longrightarrow ZnS$$

Sulphur combines slowly with hydrogen to form the gas hydrogen sulphide, H_2S. This compound is a very important reagent in chemical analysis where it is used in the precipitation of sulphides (see Chap. 38).

$$H_2 + S \longrightarrow H_2S$$

At low temperatures sulphur does not combine with oxygen, but at high temperatures it forms sulphur dioxide. Under the action of a catalyst sulphur dioxide will combine with further oxygen and form another oxide, sulphur trioxide, SO_3 (see Chap. 20).

Sulphur combines with carbon in the form of coke to form carbon disulphide, CS_2. This reaction requires the high temperatures of the electric furnace. Carbon disulphide is a volatile liquid which is used as a solvent for waxes, resins, oils, rubber, phosphorus and sulphur itself.

$$C + 2\ S \longrightarrow CS_2$$

6. Uses of sulphur. Sulphur is used principally for the production of sulphuric acid and for many years has been used in the manufacture of gunpowder. In conjunction with lime it is used as a fungicide in agricultural sprays.

An important use of sulphur is in the vulcanization of rubber. Rubber has been known for centuries and early explorers reported that natives were using crude rubber gum to make rough shoes and garments. At the beginning of the nineteenth century Charles Macintosh developed a process for making water-proof clothing, but the early garments

proved to be too sticky in summer and too brittle in winter. In 1839 Charles Goodyear found accidentally that heating a little sulphur with the rubber produced a material that could be used satisfactorily. He named this process *vulcanization* and found that by varying the quantity of sulphur he could produce a rubber of different properties. These new varieties of rubber could be used for many purposes.

Sulphur forms many interesting and important substances in combination with compounds of carbon and is used in the manufacture of dyes and drugs such as the *sulpha* compounds.

SULPHUR DIOXIDE

7. Occurrence of sulphur dioxide. Sulphur dioxide is one of the gases produced by volcanic action and is found in the neighbourhood of volcanoes. Since sulphur is present in many forms of coal, sulphur dioxide is present in the flue gases from most industrial plants. You may have noticed that in a city on a winter morning certain weather conditions which allow the smoke to cling to the ground level produce a suffocating sensation. This is due to sulphur dioxide. The gas is also produced by the smelting of some metallic ores, and the presence of this gas in the vicinity of a smelter is frequently shown by the absence of vegetation in the neighbourhood. Operators of smelters are often compelled to take steps to prevent this gas from escaping from their chimneys.

8. Preparation of sulphur dioxide.

A. Laboratory methods.

(1) *By treating a sulphite with an acid.* If sodium sulphite or bisulphite is placed in a flask arranged as shown in Fig. 72 and hydrochloric acid is added, gentle heating will cause the evolution of sulphur dioxide. Since the gas is quite soluble in water it cannot be collected by means of a pneumatic trough but is collected by the upward displacement of air, as in the case of carbon dioxide.

$$Na_2SO_3 + 2\ HCl \longrightarrow 2\ NaCl + H_2O + SO_2$$

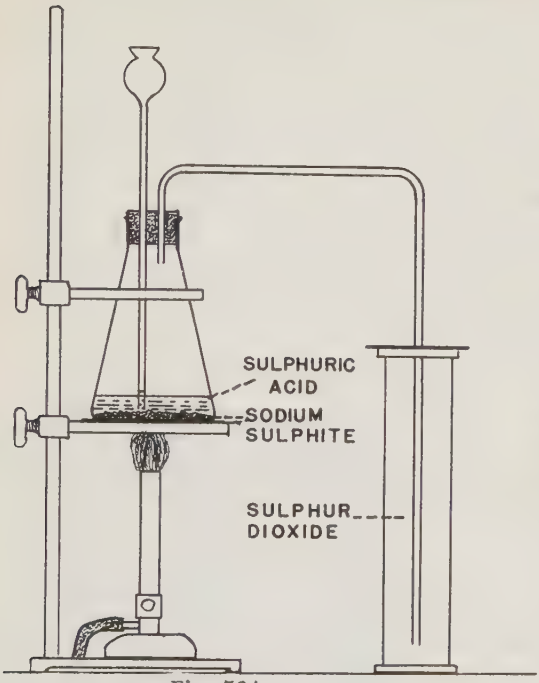


Fig. 72A.

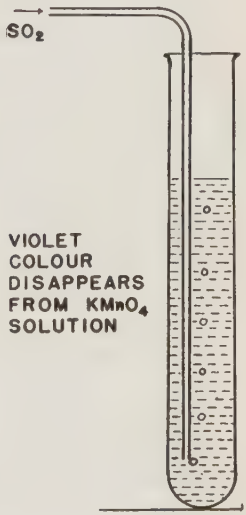


Fig. 72B.

Fig. 72. Preparation and testing of sulphur dioxide.

Note the similarity to carbon dioxide in the reaction and in the method of collection of the gas (see Chap. 13, sec. 13).

(2) *By the action of hot concentrated sulphuric acid on a metal.* If concentrated sulphuric acid and copper turnings are heated in a flask arranged as shown in the previous figure, sulphur dioxide will be produced.

$$Cu + 2\ H_2SO_4 \longrightarrow CuSO_4 + 2\ H_2O + SO_2$$

B. Industrial methods.

(1) *By burning sulphur.* When sulphur is burned in air sulphur dioxide is produced. This is a method employed in the preparation of the sulphur dioxide used in the manufacture of sulphuric acid and sulphite pulp.

(2) *As a by-product in smelting.* When the sulphide ores of certain metals are heated in air sulphur dioxide is given off. This process is known as *roasting* (see Chap. 39).

$$2\ ZnS + 3\ O_2 \longrightarrow 2\ ZnO + 2\ SO_2$$
$$4\ FeS_2 + 11\ O_2 \longrightarrow 2\ Fe_2O_3 + 8\ SO_2$$

9. Properties of sulphur dioxide.

A. *Physical properties.* Sulphur dioxide is a colourless gas with an acid taste and a sharp suffocating odour. It is very soluble in water. The gas is easily liquefied as the critical temperature is 155°C.

B. *Chemical properties.* Sulphur dioxide will not burn or support combustion. Under the action of a catalyst it combines with oxygen to form sulphur trioxide, SO_3.

$$2\ SO_2 + O_2 \longrightarrow 2\ SO_3$$

The gas is a good reducing agent. If it is bubbled through a solution of potassium permanganate the deep purple colour of the solution will disappear. The sulphur dioxide is oxidized to sulphuric acid (see Fig. 72B)

$$5\ SO_2 + 2\ KMnO_4 + 2\ H_2O \longrightarrow K_2SO_4 + 2\ MnSO_4 + 2\ H_2SO_4$$

10. Sulphurous acid. When sulphur dioxide is dissolved in water sulphurous acid is formed. This acid is very weak and unstable and cannot be removed from the solution, as it will break up immediately.

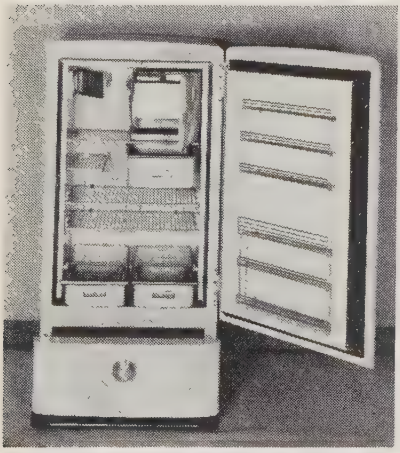
$$SO_2 + H_2O \longrightarrow H_2SO_3$$

Note the similarity between sulphurous acid and carbonic acid with respect to their preparation, strength and stability. Sulphurous acid is dibasic. It forms the normal salts, the *sulphites*, e.g., Na_2SO_3, and the acid salts, the *bisulphites*, e.g., $NaHSO_3$.

11. Uses of sulphur dioxide. Sulphur dioxide is used extensively for the production of sulphuric acid and for bleach-

ing textiles, wood pulp, straw, dried fruits and vegetables. In bleaching, the gas or its solution in water, sulphurous acid, either acts as a reducing agent, or it produces colourless and somewhat unstable addition products with the colouring materials. Newsprint and straw which has been bleached with sulphur dioxide will gradually turn yellow as these addition products break up or oxidation occurs. This explains the yellowing of straw hats and newspapers with age.

Sulphur dioxide destroys bacteria and is sometimes used as a food preservative. This use is not general, as some authorities consider that its presence in food is undesirable.



Courtesy Canadian General Electric Co.

Fig. 73A.

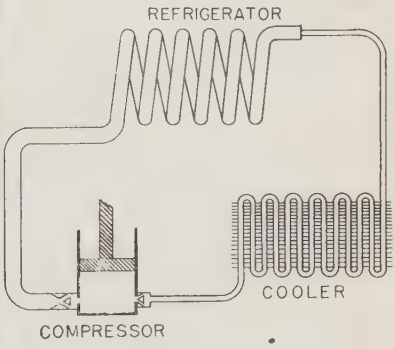


Fig. 73B.

Fig. 73. Household refrigerator and principle of operation.

Since sulphur dioxide is liquefied easily and does not attack the metal parts of the machinery it is used frequently in small refrigerator units. Fig. 73 shows a diagram of a refrigerating mechanism such as is found in homes and soda fountains.

The gas is liquefied by compression and the heat produced by the compression is removed by the cooler. The liquid sulphur dioxide is allowed to expand into the evaporator where it turns to a gas. Since evaporation is a heat-absorbing

process, heat will be taken from the surroundings—in this case, articles which have been stored in the refrigerator. The gas is then returned to the compressor and the cycle is repeated.

HYDROGEN SULPHIDE

12. The occurrence of hydrogen sulphide. Hydrogen sulphide is produced during the decay or the destructive distillation of organic substances containing sulphur. It is found in the gases from volcanoes, in the gases obtained from the distillation of soft coal, and in sewer gas. The decomposition of eggs produces the gas, and it is found in solution in certain mineral waters.

13. Preparation of hydrogen sulphide. Hydrogen sulphide is usually prepared by the action of ferrous sulphide with either hydrochloric or sulphuric acid.

$$FeS + 2\,HCl \longrightarrow FeCl_2 + H_2S$$
$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$

The apparatus used is similar to that used for the preparation of hydrogen except that the gas is collected by the upward displacement of air. It is shown in Fig. 74.

Since hydrogen sulphide is used frequently in chemical analysis it is convenient to have a method of generating it when it is required. A convenient form of apparatus is the *Kipp* generator which is shown in the diagram in Fig. 75.

The ferrous sulphide is placed in the centre part of the vessel and dilute acid is poured into the upper part. The acid fills the lower vessel and reaches the ferrous sulphide by means of the constriction between the two parts of the apparatus.

The pieces of ferrous sulphide cannot pass through the small annular opening. As soon as the acid reaches the ferrous sulphide the action commences and hydrogen sulphide is produced. The gas may be withdrawn by means of the stopcock on the side of the centre portion of the apparatus. When the stopcock is closed the increasing gas pressure will force the acid away from the ferrous sulphide and the action will cease. The gas pressure will force the acid up the centre tube into the upper part. If the stopcock is now opened the gas will be forced out by the pressure

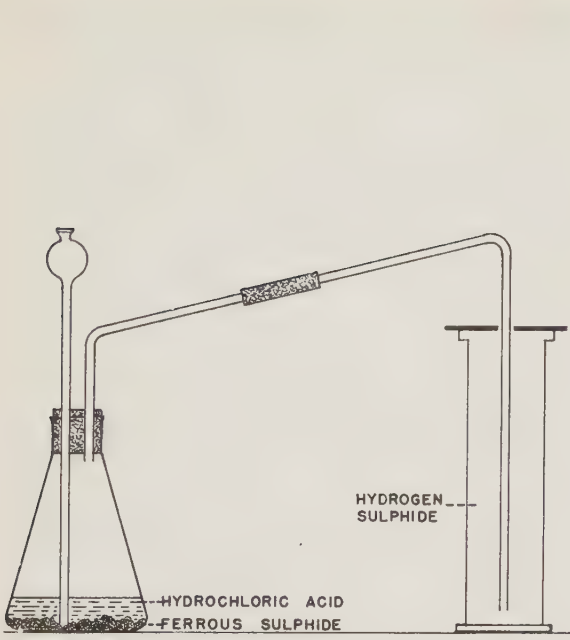


Fig. 74. Fig. 75.

Fig. 74. Preparation of hydrogen sulphide.
Fig. 75. Kipp generator.

caused by the height of the liquid. When the pressure falls enough the acid will come again into contact with the ferrous sulphide and the action will recommence. This apparatus is satisfactory for the intermittent use of small quantities of the gas, but a disadvantage is that the acid becomes diluted by the ferrous chloride which is formed and small pieces of ferrous sulphide will fall into the lower part, causing an undesired action.

14. Properties of hydrogen sulphide. Hydrogen sulphide is a colourless gas with the disagreeable odour of rotten eggs. The gas is about 1.2 times as heavy as air and is very soluble in water. It is quite poisonous and all work with the gas must be done in a well-ventilated hood. In cases of poisoning the antidote is dilute chlorine gas.

Hydrogen sulphide is not very stable and when heated will decompose.

$$H_2S \longrightarrow H_2 + S$$

Hydrogen sulphide will burn in the air, producing water and sulphur dioxide.

$$2\ H_2S + 3\ O_2 \longrightarrow 2\ H_2O + 2\ SO_2$$

Strangely enough, many people are not aware that the gas will burn, and some explosions have occurred in laboratory hoods where a high concentration of the gas had accumulated. The gas is a good reducing agent, as is shown by the following reactions:

$$SO_2 + 2\ H_2S \longrightarrow 2\ H_2O + 3\ S$$
$$2\ HNO_3 + 3\ H_2S \longrightarrow 4\ H_2O + 2\ NO + 3\ S$$
$$2\ FeCl_3 + H_2S \longrightarrow 2\ HCl + 2\ FeCl_2 + S$$

All the metals of the electrochemical series (see Chap. 38) down to and including silver react with hydrogen sulphide to form sulphides. The tarnish which appears on silverware is silver sulphide produced by the hydrogen sulphide in coal smoke.

$$2\ Ag + H_2S \longrightarrow Ag_2S + H_2$$

15. Hydrosulphuric acid. When hydrogen sulphide dissolves in water it forms a dibasic acid, *hydrosulphuric acid*, whose salts are the *sulphides* and the *bisulphides*. Most of the sulphides are insoluble in water and are precipitated from solutions of salts by passing in gaseous hydrogen sulphide.

If an aqueous solution of hydrogen sulphide is allowed to stand, the oxygen of the air will displace the sulphur which will appear in the form of a fine white precipitate.

$$2\ H_2S + O_2 \longrightarrow 2\ H_2O + 2\ S$$

Question Summary

1. Can you suggest why sulphur was used by the alchemists?
2. How does sulphur occur on the earth?
3. (*a*) How is sulphur obtained in Sicily?
   (*b*) Describe the production of sulphur in the United States.

4. (*a*) Describe the changes which occur when sulphur is heated in a test tube.
(*b*) How may the amorphous variety of sulphur be obtained?

5. (*a*) Describe the compounds which sulphur forms with oxygen and with hydrogen.
(*b*) Describe the action of sulphur with other elements.

6. (*a*) What is meant by vulcanization of rubber?
(*b*) Name various uses for sulphur.

7. Where does sulphur dioxide occur?

8. (*a*) Describe and write the equation for a laboratory method of producing sulphur dioxide.
(*b*) Describe the industrial method of obtaining sulphur dioxide.

9. (*a*) Give the physical properties of sulphur dioxide.
(*b*) Give the chemical properties of sulphur dioxide.

10. Describe the production of sulphurous acid. In what ways is it like carbonic acid?

11. (*a*) Describe the use of sulphur dioxide in refrigeration.
(*b*) Name some other uses for sulphur dioxide.

12. How does hydrogen sulphide occur in nature?

13. (*a*) How is hydrogen sulphide prepared?
(*b*) Describe the operation of a generator for hydrogen sulphide.

14. (*a*) What are the physical properties of hydrogen sulphide?
(*b*) What are the chemical properties of hydrogen sulphide?

15. What are the properties of hydrosulphuric acid?

Problems

1. What volume of sulphur dioxide at S.T.P. will be obtained by burning sulphur with 200 litres of oxygen?

2. What volume of sulphur dioxide at S.T.P. will be obtained from 150 grams of sodium sulphite by heating it with hydrochloric acid?

3. What volume of sulphur trioxide at S.T.P. will be obtained from 500 litres of sulphur dioxide?

4. How many grams of hydrochloric acid, 37% pure HCl, will be required to produce 700 grams of sulphur dioxide from sodium sulphite?

5. How many grams of copper will be required to react with 400 grams of 98% sulphuric acid to make sulphur dioxide?

Chapter **15**

Modern Ideas About Atoms and Molecules

1. Introduction. Learning the story of matter is much like watching the growth of a tree. A tiny sapling has only a very few leaves and you can see it all. Then branches appear and it becomes necessary to explore each part if you wish to know the whole tree in detail. We have tried to do the same thing with matter. At first our knowledge was so scanty that men tried to explain matter by a single theory; then they sought to explain separate behaviourisms such as combustion; later they sought to understand more accurately only the gaseous states of matter. As they learned more about the chemical alterations in matter they came to the conclusion that it was made of particles, and they deduced the relative weights of these particles. They even learned to describe their attraction for one another and identified the individual types of atoms which are represented by symbols. They slowly deduced the composition of more complex types of substances and learned how to make accurate predictions about chemical changes. This is where we are now.

As this story goes on we will explore many more branches in some detail. We should have a glance ahead now and get a bird's-eye view of what man thought about the nature of matter generations later than the present stage of our story because it helps us to see where we are travelling.

2. A theory about the three states. Have you ever wondered how the three states of matter are related and why they behave the way they do? You know that a gas can

be compressed and that it will expand indefinitely if the walls are continually moved back. You know it will diffuse throughout other gases until it is uniformly distributed among them. You also know the precise laws which were discovered about each of these properties. You know that liquids flow and take the shape of the containing vessel, that solid metals will bend and may be drawn into fine wires or rolled into thin sheets.

All the properties of the three states are explained by the hypothesis that matter is made of discrete particles called atoms and molecules, and you have seen how men deduced their existence. To explain the behaviour of matter it is necessary to define the nature of those particles more exactly. The first step is the kinetic-molecular theory.

3. The Kinetic-Molecular theory. This theory postulates that all molecules and atoms are in motion of some kind if their temperature is above absolute zero. The molecules are considered to be of very minute, but finite, dimensions. The molecules are relatively very far apart in the gaseous state and they are dashing about madly in the empty spaces. Since they are so tiny their sphere of attraction is too small for them to affect each other in the gas. In addition, it is assumed that when these minute bodies collide with one another or with an object at the same temperature, there is no loss of energy. We say the collisions are perfectly elastic. They strike one another and the walls of the containing vessel but they do not dissipate their energy in friction. At any selected temperature and pressure the average velocity of all the molecules of any one kind is constant, but some are moving very rapidly and others are almost stopped.

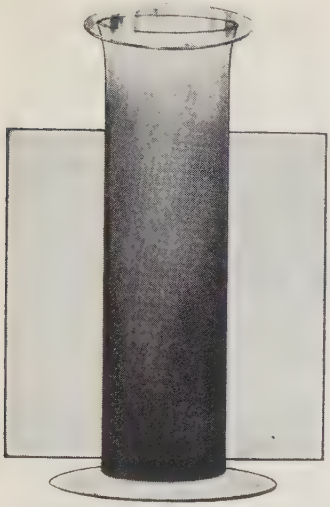
4. Gases. The behaviour of gases may be explained readily by this theory:

(*a*) *Compression and expansion.* As early as 1740 Bernoulli suggested that the pressure of a gas is due to the impact of its

particles upon the walls of a vessel. Over one hundred years later mathematical scientists proved that he must be correct. Since each molecule is independent of every other molecule, compression merely shoves them into a smaller space. In the smaller space they are closer together and more of them collide with each unit area of the wall so the pressure increases as the volume decreases. This is Boyle's Law. As the walls are withdrawn a gas expands indefinitely because there is no limit to the space which may exist between the molecules.

(*b*) *Expansion and contraction with temperature.* An increase in temperature makes the molecules move more rapidly and thus they strike the walls oftener and harder. This increases the pressure and if it is to be kept constant on any given mass of gas the volume must be allowed to increase. This is the explanation of Charles' Law.

(*c*) *Diffusion.* It is simple to understand why one vapour diffuses throughout another if the molecules move independently among one another. Hydrogen diffuses most rapidly since, being so light and having its molecules possessing the same energy as other molecules at the same temperature, they must travel very fast. The average velocity of its molecules at 0°C. is over 2000 yards a second or nearly 70 miles per minute so its molecules travel at what we call supersonic speeds. Since molecules move so very fast it is easy to understand why foul odours or pleasant scents travel through the air and finally disappear by dilution. However, molecules are so numerous at ordinary pressures that a molecule collides with its neighbours about 150,000 times while it travels one inch. This means that in a mixture all the molecules of different kinds have the same *average* energy. Now the rate of travel is inversely proportional to the square root of the mass for molecules with the same energy, so this is the law of diffusion.



From Black & Conant: "New Practical Chemistry", courtesy The Macmillan Company.

Fig. 76. Diffusion of bromine in air.

Courtesy Fisher Scientific Co.

Fig. 77. Thomas Graham, Scottish chemist known for his Law of Diffusion (1829) and his work on colloids (1861-2).

(*d*) *Other properties.* All the properties of gases may be explained with great precision by means of this theory and it has become a great branch of science. Avogadro's number, Dalton's Law of Partial Pressures, liquefaction and a host of other peculiarities of gaseous behaviour, become understandable.

5. Liquids. Liquids, unlike gases, are virtually incompressible. This would lead us to conclude that the molecules are almost touching, if not actually in contact. They have room enough to shift places rather easily because the less viscous liquids quickly take the shape of their containers. The molecules are so close together that the attraction between them prevents any but the ones of highest energy from escaping. Still, molecules of liquids are in motion as is shown by the diffusion of liquids in liquids or solids in liquids.

The fact that liquids evaporate more rapidly at higher temperatures is explained by the fact that the average energy

of the molecules is greater, and a larger proportion can escape from the attraction of their fellow molecules. The evaporation and condensation of liquids in a closed space is one of the best examples of a state of dynamic equilibrium. Suppose a drop of water, benzene, ether or some other liquid, is put into a barometer tube by means of a medicine dropper with a curved tip. If a condenser jacket is placed around the barometer tube, water at any temperature may be passed through the condenser. The average kinetic energy of the liquid molecules at any temperature is constant but some individuals have excess energy and some have a deficiency. Some of the high-energy molecules can overcome the surface attraction and escape into the vapour space. This is *evaporation* and it occurs continually at a liquid surface. The molecules which have evaporated are in the gaseous state and are exerting pressure on all surfaces. This is the *vapour pressure*. The paths followed by some of the molecules will lead them back to the liquid surface where they may be recaptured. This is *condensation*. When evaporation commences the number of molecules per millilitre in the vapour state is small and the number escaping from the surface per second is greater than the number returning. A concentration in the vapour is soon reached *when the number of molecules recaptured per second is equal to the number lost per second from the surface*. A *dynamic equilibrium* has been established. Both evaporation and condensation continue to occur but they do so at rates which balance one another as long as the temperature is constant.

If the tube is warmed the average kinetic energy of the molecules of the liquid is increased and more molecules escape per second than can return. The equilibrium adjusts itself until a new vapour pressure has been established and the mercury falls still farther in the tube. The increase in the vapour space in the tube is a measure of the increase in the vapour pressure. These vapour spaces are shown in

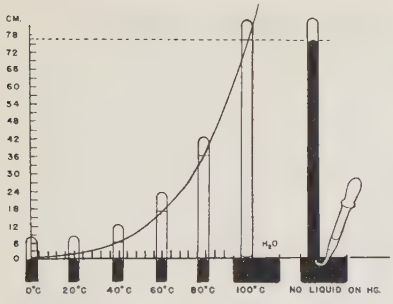
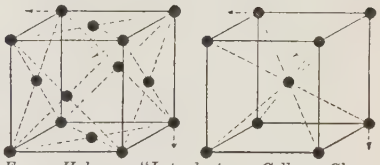


Fig. 78. Vapour pressure of water at different temperatures.



From Holmes: "Introductory College Chemistry", courtesy of The Macmillan Company.

Fig. 79. Face-centred and body-centred cubic crystals.

order in Fig. 78, so as to make a graph of the variation of the vapour pressure with the temperature. *The vapour pressure* or vapour tension of any substance is the *equilibrium pressure exerted by the molecules of that substance at a given temperature in a closed space.* The vapour pressures are shown in Table 13.

TABLE 13—VAPOUR PRESSURE OF WATER

Temp. °C.	*Pressure* (*mm. of Hg*)	*Temp.* °C.	*Pressure* (*mm. of Hg*)	*Temp.* °C.	*Pressure* (*mm. of Hg*)
0	4.60	22	19.83	60	149.4
10	9.21	24	22.38	70	233.7
12	10.52	26	25.21	80	355.1
14	11.99	28	28.35	90	525.8
16	13.63	30	31.82	95	633.9
18	15.48	40	55.32	100	760.0
20	17.53	50	92.51	110	1074.6

6. Solids. The kinetic theory pictures solids as composed of molecules or atoms arranged in a pattern in space (see Fig. 79). They have enough room to vibrate but they cannot roll around one another except under great stress.

This theory has been verified magnificently by means of X-rays. The rows of atoms in crystals act as diffraction gratings to scatter these very short wave lengths of radiation and men have learned to deduce the positions of the atoms in the crystals from the X-ray patterns.

The external shape of the crystals can be related to the planes of atoms in the lattice-like structure. The external geometrical forms of crystals may be divided into the six systems shown in Fig. 80.

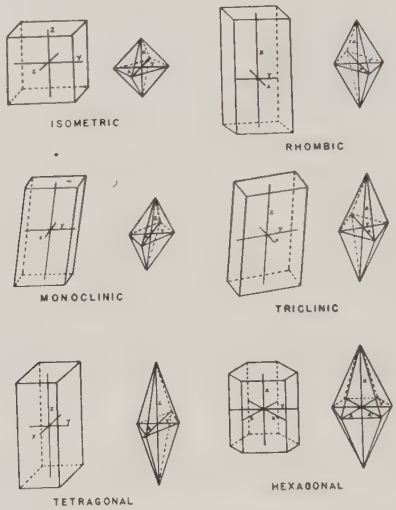


Fig. 80. The six systems of crystal symmetry.

7. Atoms are not indivisible. Dalton, like the early Greek thinkers, believed the atom to be a small hard indivisible unit of matter. In 1859 Plucker discovered that when nearly all the gas in a glass tube with metal electrodes at each end has been pumped out it conducts electricity and the remaining gas glows. His discovery is used every day in the familiar neon signs. Sir William Crookes showed that there was a stream of negative particles flowing toward the positive terminal and these were later called *electrons*. It was soon shown that they came from the atoms and molecules of gas in the tube. The remaining positive parts of the atoms and molecules flowed to the negative electrode. In Topic VI we will review some of the steps by which men proceeded to deduce the structure of the whole atom.

It was shown by later experiments that the atoms were mostly empty space and the weight must be concentrated in a very small *nucleus* containing all the positive charges. By studying the wave lengths of the light emitted by these gases in a discharge tube it was possible to calculate how the electrons were distributed about the nucleus of the atom. The simplest concept, due to Niels Bohr, is that electrons have definite energy contents and the higher the energy of an electron the greater the size of the orbit in which it revolves about its nucleus. We also know that there can be only a limited number of electrons in each orbit or energy level. There can be two electrons in the orbit nearest to the nucleus, eight in the next orbit and eighteen in the third orbit. The outermost orbit, however, tries to secure eight electrons so if the third orbit happens to be the outermost one it may be stable with eight electrons.

The nucleus has a positive charge which increases from element to element with the number of electrons which revolve around it as planets revolve about the sun. We find that the hydrogen nucleus has unit weight and a unit positive charge. It is called a *proton*. The helium nucleus has a double positive charge, but helium has an atomic weight of 4 so it is concluded that it consists of two protons and two uncharged particles of unit atomic weight called *neutrons*. The third element, lithium, has a nuclear charge of three units. Beryllium has a charge of four, boron has five, carbon has six, nitrogen has seven, oxygen has eight, and fluorine has nine units of positive charge on its nucleus. These numbers are called the *atomic numbers* of the elements because they give the charge on the nucleus in the order of their increasing atomic weights.

We can now build up diagrammatic pictures of the structures of the various atoms in terms of their constituent parts as is done in Fig. 81.

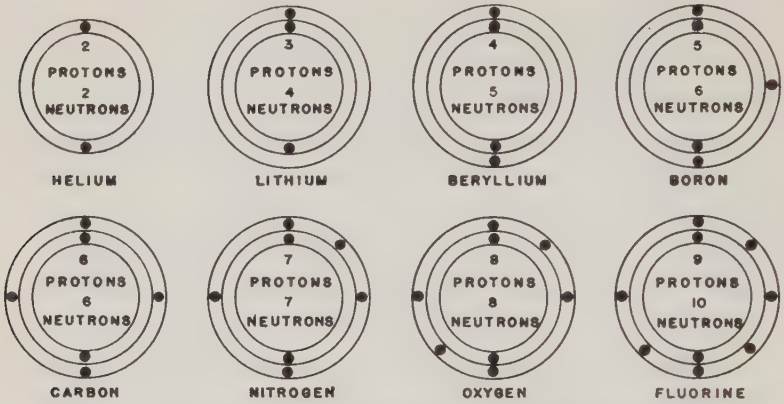


Fig. 81. Electron arrangements in some of the lighter atoms.

This would seem to require that all the atomic weights should be whole numbers but the explanation of this old riddle was soon found. By a study of the positive ion rays it was found that those atoms which had fractional atomic weights had two or more different kinds of nuclei inside similar planetary electron arrangements. Since the electrons are on the outside they determine the chemical properties. There are thus two kinds of lithium atoms—one kind with

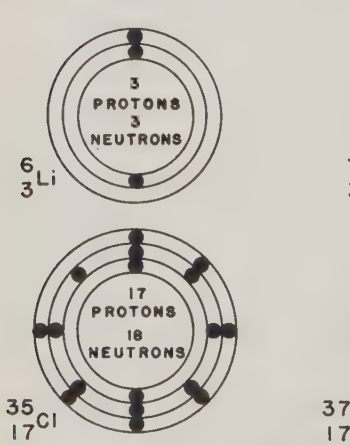


Fig. 82. Two kinds of lithium atoms and two kinds of chlorine atoms.

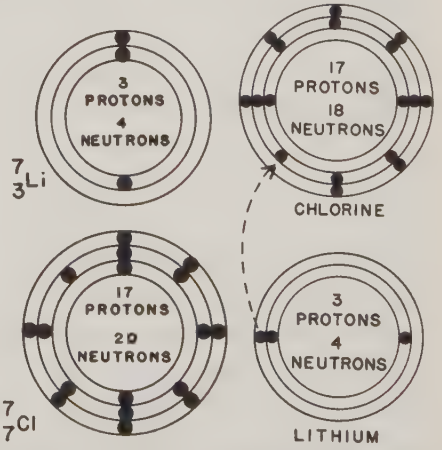


Fig. 83. How lithium chloride forms.

an atomic weight of six units and one with an atomic weight of seven units. These *atoms which have the same atomic number but different atomic weights* are called *isotopes*. The lithium isotope having a mass of seven units is more abundant than the one with six units of mass. We usually find that about 94 per cent of the atoms of lithium have a mass of seven and only 6 per cent have a mass of six. This gives an average atomic weight of 6.94. The diagrammatic structure of these isotopes is shown in Fig. 82. Other elements have isotopes in such proportions as to give them the accepted average atomic weights.

8. Why atoms react chemically. Now we can understand the formation of chemical compounds. If an atom or radical has an *excess of electrons* it is a *negative ion*. If it has a *deficiency of electrons* it is a *positive ion*. When it has equal numbers of positive and negative charges as in a normal atom it is neutral. Note that the positive charges are bound up in the nucleus and *only electrons are lost or gained*. Metallic atoms and hydrogen atoms tend to lose some of their outer electrons. This leaves them as positive ions. Thus:

$$\mathbf{Na^{\circ} - 1\ electron \longrightarrow Na^{+}}$$

The sodium ion has a deficiency of one electron. The chlorine atom, on the other hand, tends to gain an electron to go with the seven electrons already in the outer shell. This gives the chloride ion an excess of one electron:

$$\mathbf{Cl^{\circ} + 1\ electron \longrightarrow Cl^{-}}$$

This is illustrated in Fig. 83.

Particles with opposite electric charges *attract* each other so these ions will quickly arrange themselves into a lattice where oppositely charged particles are as close together as possible. It is obvious that if sodium and other metal atoms tend to lose electrons while oxygen, sulphur, chlorine

and other non-metal atoms tend to gain them they will exchange electrons between their outer shells and then the oppositely charged particles will attract one another. This is the simplest type of chemical affinity. We will learn about other types in Chap. 32.

9. Energy in chemical changes. The great basic reason for all these transfers of electrons and consequent chemical changes is that atoms and molecules move into a more stable energy state by the change. Every substance tries to exist in the lowest energy state just as water seeks the lowest level. Certain numbers of electrons appear to be more desirable than other quantities in the outer shells of atoms and they make arrangements to secure these numbers in their outer shell in order to go to a lower energy state.

The liberated energy may appear as heat, light, electricity, or other forms of energy. Spontaneous chemical changes always involve a liberation of energy in some form. A great deal of such energy may appear as heat. If a reaction gives out heat we say it is *exothermic*; if it goes on with the absorption of heat energy we call it *endothermic*. We often cause chemical changes which are not in themselves spontaneous by supplying the energy from outside sources.

Question Summary

1. List some of the questions left unanswered by the older atomic-molecular theory.

2. Enumerate some of the facts about the three states of matter which must be explained by any hypothesis about matter.

3. State briefly the kinetic-molecular picture of matter.

4. Describe briefly how the kinetic-molecular theory explains the expansion, compression and diffusion of gases.

5. (*a*) Give the kinetic-molecular view of the liquid state and some of its properties, such as vaporization and condensation.

(*b*) Explain carefully why the equilibrium vapour pressure occurs with a fixed value at each temperature.

6. In what way are X-rays used in studying the structure of matter?

7. (*a*) What is our present-day view of Dalton's indivisible atoms?
(*b*) How are simple ions formed from atoms?

8. (*a*) How is simple chemical combination explained by the electron theory of matter?
(*b*) Illustrate by diagrams how the following ions and ionic compounds are formed by the transfer of electrons: H^+, F^-, Mg^{++}, $S^=$, $MgCl_2$, Li_2O, HCl.

9. (*a*) What causes chemical change?
(*b*) Why would one atom substitute itself for another atom in a compound?

10. Review Question
Define or explain the following terms: exothermic, isotope, proton, atom, molecule, neutron, nucleus, kinetic, planetary, electron, endothermic, amorphous, crystalline, radicals, vapour pressure, evaporation, dynamic equilibrium.

Topic Three

MATTER IN MOTION APPEARS AT REST

When scientists had explained the nature of many chemical changes and determined the structure of pure substances they sought to understand why some reactions are rapid and some interminably slow, why some produce large yields of products and others stop far short of completion. By studying the factors which affect the speed of reactions they deduced the role of energy in driving reactions forward or backward as well as the influence of purely physical consequences such as solubility. This knowledge of reaction rates and their relation to the equilibrium state laid the basis for new and improved manufacturing processes. Our vast heavy chemical industry uses these laws and principles to determine the optimum conditions for producing many of the chemicals we use most often. Some of the applications are described in this topic.

REACTION RATES AND EQUILIBRIUM

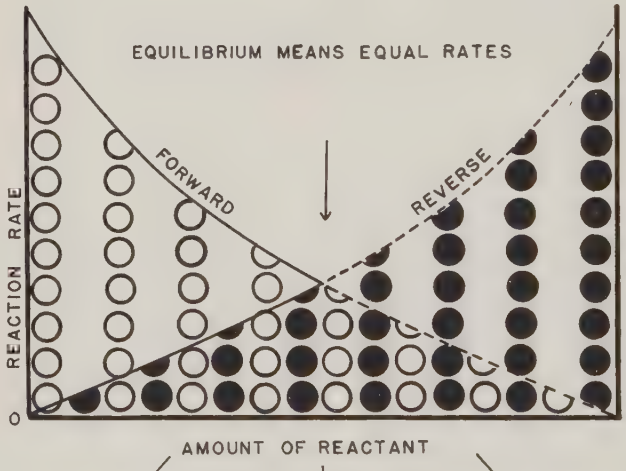
FORWARD REACTION RATE DEPENDS UPON

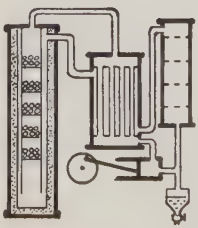
1. NATURE OF REACTANTS
2. TEMPERATURE
3. PRESSURE OR CONCENTRATION
4. CATALYSTS

REVERSE REACTION RATE DEPENDS UPON

1. NATURE OF PRODUCTS
2. TEMPERATURE
3. PRESSURE OR CONCENTRATION
4. CATALYSTS

PRINCIPLE OF LE CHATELIER
LAW OF MASS ACTION



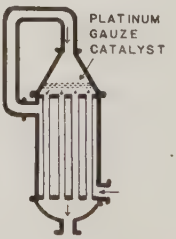


HABER PROCESS

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

CONTACT PROCESS

$2SO_2 + O_2 \rightleftharpoons 2SO_3$



OSTWALD PROCESS

$NH_3 + 2O_2 \rightleftharpoons HNO_3 + H_2O$

Chapter 16

The Velocity of Reactions

1. Introduction. In practical affairs we are often more interested in *rates* of change than we are in their explanation. We are more concerned with how fast T.N.T., R.D.X. or dynamite will explode, than we are in their nature or the vast volumes of gases they will produce. In everyday life we are nearly all concerned in some way with the factors controlling the combustion of fuel.

2. Factors in controlling rates of reaction. By the *rate of a reaction* we mean the speed with which some resultant is formed or some reactant is used up. To be exact it has to be measured in mols or molecules transformed or produced in a unit of volume per unit of time. We have already considered the factors influencing the rate of reactions in Chap. 5, sec. 7.

Chemical reactions, in the ultimate sense, are simple mechanical processes between atoms and molecules. Individual atoms must get together in actual proximity to one another, at a time when each is in the proper energy state, before they can react. Reaction does not occur between every group of reactive particles merely because they all happen to come together at one time but it occurs if they all *collide and have the necessary energy of activation* at the same time. Atoms or groups of atoms which carry charges, i.e., ions, may be said to be sufficiently activated but only a small proportion of normal atoms or molecules will be likely to possess abnormal energies at any one time. The proportion increases with the temperature.

The physical factors which determine the speed of a reaction do one or both of two things:

(*i*) They alter the rate of contact of individual particles.
(*ii*) They change the proportion of the particles which are capable of reaction.

In any specific case the rate depends upon:

(*i*) *The nature of the reactants.* Sodium reacts rapidly with water but magnesium displaces hydrogen from water very slowly at the same temperature. Each reaction has a characteristic rate factor which is determined by the reactants involved.

(*ii*) *The degree of subdivision of liquid and solid reactants.* Only the molecules in the surfaces or interfaces can come in contact. Substances react much more quickly in solution because the reacting substances are at least molecularly dispersed. The reaction rate in solutions is controlled by how close the molecules are to one another, since their surface is a maximum.

(*iii*) *The concentration of the reactants.* This applies to solutions or homogeneous mixtures where the number of reacting particles per unit volume is uniform. The greater the number of particles per unit volume, the greater is the number of collisions per unit volume and the greater the reaction rate. We will soon learn more precise rules about the influence of this factor.

(*iv*) *The temperature.* You will recall that the addition of heat energy increases the rate of movement of particles. As the speed increases the number of collisions per unit of time is increased and also the proportion of the molecules which have the necessary energy of activation. The specialists in kinetic theory say there are more fruitful collisions per unit volume. No exact general rule can be stated about the effect of temperature but a rise of 10°C. will often double or triple the velocity of a reaction.

(*v*) *The surroundings, such as solvents and catalysts.* Some solvents are better dispersing agents than others and they promote reactions by increasing the contact area. It is well known that the presence of traces of impurities often multiplies the speed of reactions many times. You know that less than one per cent of manganese dioxide or ferric oxide mixed with potassium chlorate will increase the rate of decomposition many times and allow it to take place at a lower temperature. Substances which affect the speed of reactions in this way are called *positive catalysts*. It appears that catalysts may facilitate the rate of contact of particles or reduce the activation energy or both, but whatever their mechanism of action they are remarkably effective.

(*vi*) *The action of light and radiant energy.* Since a reaction is often dependent upon the acquisition of an abnormal amount of energy by one or more of the reacting particles it is not surprising that some reactions are accelerated if any of the reactants can directly absorb radiation. Hydrogen and chlorine may be kept together in the dark and they combine very slowly but if brought into bright sunlight the reaction may be explosive. The most important chemical reaction for the maintenance of life on this planet is one of these photochemical reactions—the synthesis of starch from carbon dioxide and water by a green leaf in sunlight. It is called photosynthesis. The taking of pictures depends on the photochemical decomposition of silver halides by exposure to light of various wave lengths. X-rays, ultra-violet radiation, radar waves, infra-red rays, and other radiations have all been used to accelerate reactions.

(*vii*) *Electrical discharges or radioactive emanations.* Atoms and molecules may be activated by colliding with an electron or other charged particles. Ozone is produced when a discharge of electricity occurs in air, as in a lightning flash.

3. The effect of concentration. In order to speak generally about all kinds of compounds at once we may call them by letters instead of names and formulas. Let us designate two reactants by the letters A and B and the resultants they produce by the letters C and D. A and B are represented in the diagram by black and white dots respectively; we are trying to picture how a change in concentration will affect the rate at which they will react when the temperature, the surroundings and all other factors are constant. We may begin by considering a reaction where one molecule of A reacts with one molecule of B. .This is called a *bimolecular* reaction. It is much simpler pictorially if we also assume that A and B are present in equal numbers.

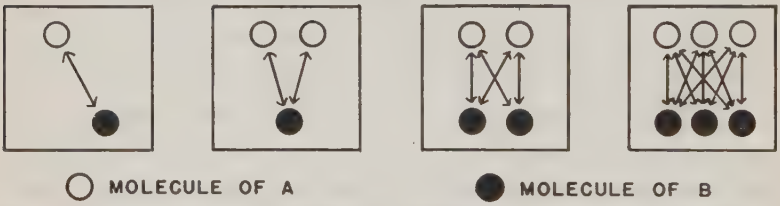


Fig. 84. The speed of a reaction is proportional to the concentration of each kind of molecule.

If a molecule of A is to combine with a molecule of B they must first come into contact. Let each square in Fig. 84 represent a very minute unit volume. If the concentration of A is doubled there are twice as many molecules per unit volume and, as you can see, the chance of an A-B collision is doubled and the rate of the reaction is also doubled. If A is not doubled but B is doubled the chance of collision is doubled and the rate of reaction is again twice as great. Each double-headed arrow represents one possibility of collision. If the concentrations are each tripled the rate of reaction will be increased ninefold. *The transformation of a reactant in a chemical reaction is speeded up in proportion to its concentration and also in proportion to the concentration of all the*

other reactants involved in the chemical change. We say in chemical jargon that the forward reaction is speeded up by the presence of more active masses. For this reason the effect of concentration described here is known as the *Law of Mass Action.* The concentration is one method of measuring the active masses of the reactants. This *Law of Mass Action* was proposed by Guldberg and Waage about 1867 and it is the basic law governing the rate of chemical change with concentration under any given set of conditions. It is fundamentally important in the study of industrial processes, physiology, chemical analysis, medicine and all places where chemical changes occur.

4. The effect of pressure on gas reactions. In a gas at atmospheric pressure the molecules are relatively very far apart and the kinetic theory tells us that pressure forces them closer together. This will increase the rate of collision and hence the rate of reaction. Solids and liquids are virtually incompressible so their reaction rates are little influenced by pressure. In a gaseous reaction we may use partial pressures instead of concentrations because all gases have the same number of molecules in equal volumes at the same temperature and pressure. This means that the number of molecules of each kind is proportional to the partial pressure. For a gaseous reaction between A and B we may say that the speed of the transformation will vary as the product of the partial pressures of the reactants.

5. Catalysis. While the law of mass action tells us how the concentration will affect the velocity of a reaction under a given set of conditions, we can often do a great deal about the conditions by choosing the correct catalyst. This is because catalysts are the submicroscopic mechanical tools by which new products are made in a minimum of time. It almost appears as if a reaction never occurs without some substance acting as a third party to the change. The reactions of life in plants and animals, the production of chemicals,

and the processes of nature all seem to have their individual accelerators or controllers.

There are certain general things about all catalytic action which you should keep in mind:

(*i*) A catalyst *affects the speed* of reaction between certain substances and also the speed of the reaction between their products. Positive catalysts increase the speed. Negative catalysts or inhibitors decrease the speed.

(*ii*) The catalyst is *not consumed* in the reaction.

(*iii*) The catalyst may *merely start* the reaction.

(*iv*) The catalyst *does not affect the degree of completion* of a reaction. It speeds up the attainment of the final state but does not alter its nature.

Positive catalysts are usually divided into two classes according to their mode of action. (*a*) *Contact or surface catalysts* which are unaltered in the process. (*b*) *Intermediate compound formers* which unite with one of the reactants until it can combine with the other reactant when they become regenerated to work again. The reactions with contact catalysts are usually called heterogeneous reactions because they occur at bounding surfaces, while the intermediate compound formers are homogeneous catalysts mixed uniformly with the reactants.

Contact catalysts are believed to accelerate reactions because they adsorb, or hold, the reactants in a monomolecular layer on their surfaces where they can come into close contact, react and evaporate again as products. It is thought that the adsorption so alters the reactants that the energy of activation is very much reduced, perhaps made unnecessary, or provided by the catalyst out of the energy of the reaction on its surface. You will note the use of vanadium oxide in the production of sulphur trioxide, of ferric and chromic oxides in the synthesis of ammonia, of platinum black in the oxidation of ammonia to nitric acid in this topic

and of finely divided nickel in the production of solid fats from vegetable oils (see Chap. 44, sec. 11).

Since the reactions occur only at the surface it is necessary to have the material finely divided and very porous. If its surfaces are full of fine cracks and fissures where points and corners are in multitudes it is more effective than if it has smooth surfaces. Catalysts are very specific because the reacting molecules have to fit more or less perfectly onto their surfaces before they are effective. It takes very small amounts of material to cover the surfaces with a monomolecular layer. If traces of impurities, such as water vapour, increase the activity of the catalyst they are called *promoters* but if they destroy the activity they are called *catalytic poisons.* Traces of arsenic are a powerful poison for the platinum catalysts used in industry. Charcoal catalysts are promoted by adding traces of copper, silver, or iron, which provide "active centres"; but these centres are easily poisoned by a trace of cyanide or other tightly held impurity which combines with metal.

Intermediate compound formers are substances acting as does nitric oxide in the lead chamber process for the oxidation of sulphur dioxide to sulphur trioxide (see Chap. 20, sec. 5). It is believed that many of the enzymes of plant and animal systems function in this manner in promoting chemical changes.

6. Chain reactions and explosions. In many reactions one or more activated particles are regenerated by the chemical change. When hydrogen and chlorine are placed in the light, the chlorine absorbs some radiant energy and a molecule becomes two activated atoms ready to react with the first molecule of hydrogen they strike. A series of changes then takes place.

(1) Cl_2 + **Radiant Energy** $\longrightarrow$ 2 Cl^* (**activated**).

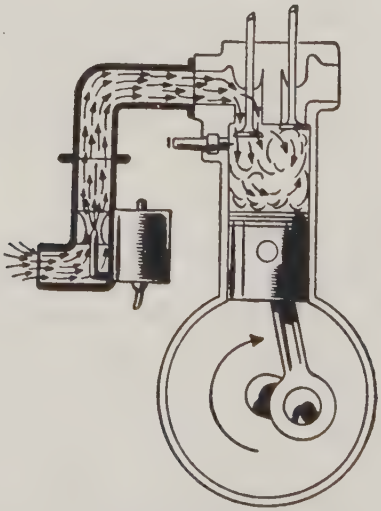
(2) $Cl^* + H_2 \longrightarrow HCl + H^*$

(3) $H^* + Cl_2 \longrightarrow HCl + Cl^*$

The third reaction provides activated atoms for the second and the second for the third and so on until the chain reaction is broken. If these chains are started at very many places the gases react with explosive violence.

Of more consequence are the chain reactions where the reaction of one molecule produces two or more activated fragments. This occurs in the oxidation of some hydrocarbon vapours such as gasoline. The number of molecules reacting is so great that within a fraction of a second the whole mass is reacting and an explosion results.

These chain reactions can be controlled. If the container of an explosive gaseous mixture is filled with glass wool the activated molecules lose their energy by collision with the fibres and the chains are largely destroyed. Many foreign substances, including lead tetraethyl, are put into gasoline to prevent the explosion from *knocking* the piston of the engine down against the wristpin. These substances cause the



From Holmes: "General Chemistry", courtesy of The Macmillan Company.

Fig. 85. Regulation of the speed of chain reactions is important in obtaining a smooth, powerful explosion.

charge to burn more slowly, shoving the piston down powerfully but smoothly. Substances like lead tetraethyl, Pb $(C_2H_5)_4$, are thus anti-knock compounds or *negative catalysts*.

Question Summary

1. In what ways are rates of reaction important?

2. (*a*) What units are needed for the measurement of reaction rates?
(*b*) What is meant by activation? What other fundamental process is involved in determining the rate of a chemical change?
(*c*) Name seven factors which may affect the speed of a reaction.
(*d*) Why are reactions in solution more rapid than the same reactions between the materials in the solid state?
(*e*) Explain why starch can cause a dust explosion but is perfectly safe in boxes or bags.
(*f*) Describe two ways in which an increase in temperature may affect the speed of a reaction.
(*g*) Why is the process of making starch in green leaves called photosynthesis?
(*h*) How could a lightning storm change the odour of the air?

3. (*a*) What is meant by molecular concentration?
(*b*) Explain how doubling the concentration of one reactant will affect the rate of reaction. What is the effect of doubling the concentration of two reactants?
(*c*) What would be the effect of trebling the concentrations of all three reactants in the reaction $A + B + C \longrightarrow D + E$?
(*d*) In the reaction $2\ NO + O_2 \longrightarrow 2\ NO_2$, what effect will the following have on the rate of formation of NO_2?
(*i*) Increasing the oxygen concentration five times.
(*ii*) Increasing the nitric oxide concentration four times.
(*e*) State the Law of Mass Action for a single reactant; for a single reaction.

4. (*a*) Explain how an increase in pressure will affect the speed of a gaseous reaction.
(*b*) What would be the effect of doubling the total pressure on the reaction $N_2 + 3\ H_2 \longrightarrow 2\ NH_3$?

5. (*a*) Why are catalysts so important in manufacturing?
(*b*) What general rules apply to all catalytic action?
(*c*) Describe two ways in which a catalyst may operate.
(*d*) What are promoters? How is a catalyst poisoned?

6. (*a*) What is meant by a chain reaction?
(*b*) What type of reaction gives rise to an explosion?

Chapter 17

Reversible Reactions and Equilibrium

1. Equilibrium is a state of nature. The energy associated with matter, like the waters of the earth, is ever seeking the lowest level. Everything tends to change until its energy is as widely uniform as possible. Temperatures tend to become uniform; pressures equalize; substances diffuse from places of higher concentration to those of lower concentration; and electric charges tend to distribute themselves evenly over conductors. These processes continue until we have a state of equality or uniformity. They go on until an *equilibrium* is established.

You have had examples of physical equilibrium. You know that the leaning tower of Pisa remains standing because opposing forces are able to keep it in stable equilibrium. You have adjusted your weight on a see-saw until it balanced that of your friend on the opposite end, and you thus brought it to an uncertain state of rest where it would tip either way if either of you should move. This was a state of *static equilibrium*. Liquids have a specific vapour pressure at each temperature because the molecules are not *static* but *dynamic*, i.e., in motion. In a closed space they continuously leave the surface of the water and steadily return from the vapour phase. When the number leaving each square centimetre of surface per second is equal to the number returning each second we say the air is saturated and a *dynamic equilibrium* has been established. No change appears to be taking place but the particles are in a state of rapid motion (see Chap. 15, sec. 5).

Another dynamic equilibrium is observed in a saturated solution. Let us note the changes in *rates* which occur during its formation. When a solute such as cane sugar is placed in some pure water the outer molecules are swept away into the solvent by the motion of its molecules and practically none of them can return. The rate of solution is thus a maximum at the beginning. As the sugar dissolves the number of sugar molecules which collide with water molecules increases and the chance of their being driven back onto the solid increases with the concentration. This is the reverse change, the deposition or crystallization of sugar from solution. The rate of deposition increases until it becomes equal to the rate of solution. To all appearances no more sugar will dissolve and we say the solution is saturated. If you could watch the change in the shape of the sugar crystals which are in contact with the solution you would realize that this is really a dynamic equilibrium where millions of molecules are exchanging places every second. Like the vapour pressure equilibrium, the amount of sugar dissolving per second increases with the temperature. At any temperature the amount in solution must be great enough to reform solid sugar crystals as fast as they dissolve.

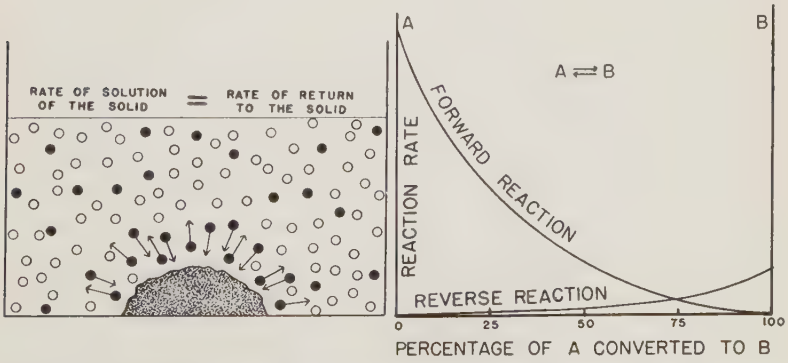


Fig. 86. At equilibrium the rate of the forward reaction has become equal to the rate of the reverse reaction.

Chemical equilibrium involves two rates of change in opposite directions. Practically all chemical reactions are reversible to some extent, even if it is very slight. This means that the resultants of a reaction continually interact to reform the reactants. When the rate of reaction becomes equal to the rate of reformation of the reactants the process of change appears to come to rest. This is only a description of dynamic equilibrium. Each reaction is unmaking the compounds formed by the other.

2. Characteristics of chemical equilibrium. Consider the classical reversible reactions first studied in great detail by Bodenstein:

$$H_2 + I_2 \underset{r}{\overset{f}{\rightleftharpoons}} 2\,HI$$

When pure hydrogen is introduced into a vessel containing iodine the rate of the forward reaction, f, is a maximum since no hydrogen iodide is present and the concentrations of both hydrogen and iodine are at their full value. The rate of the forward reaction is proportional to the product of these concentrations and as they are used up this rate decreases as shown in Fig. 86. The rate of the reverse reaction is zero at the first instant because it is proportional to the square of the concentration of hydrogen iodide. As the forward reaction proceeds the rate of the reverse reaction, r, increases as shown. If the temperature is held constant at 360°C. the rate of the forward reaction will uniformly decrease and the rate of the reverse reaction will steadily increase until they become equal. If an experimenter starts with equal numbers of molecules the reaction will reach equilibrium when about 87.5 per cent of the hydrogen and iodine have reacted. Only 12.5 per cent remains because hydrogen and iodine react to form hydrogen iodide much

more rapidly than hydrogen iodide decomposes. At 360°C. the rates do not become equal until there are about eight molecules of hydrogen iodide for each molecule of hydrogen, when the reaction is started with an equimolecular mixture of hydrogen and iodine. This proportion will only exist if we do start with equal numbers of molecules of hydrogen and iodine.

If we were to start with pure hydrogen iodide then the decomposition reaction would have a maximum rate at the very beginning. This rate would be much less than the rate of the recombination reaction because it is fundamentally slower. The latter reaction would soon pick up speed as more hydrogen and iodine was formed and when about 12.5 per cent of the hydrogen iodide was decomposed the rates of the forward and reverse reactions would be equal and equilibrium would be established again. Note that:

(1) *The same equilibrium point is reached regardless of the side from which it is approached.*
(2) *The position of the equilibrium point depends on the relative rates of the opposing reactions.*

A detailed study of equilibrium would give you two other general principles:

(3) *The equilibrium point occurs at a definite value for each temperature.*
(4) *The presence or absence of catalysts has no effect on the position of the final equilibrium point.* They alter the time required to reach equilibrium.

3. The Equilibrium Law. The most convincing classroom demonstration of the effect of mass action or concentration on the velocity of reactions is the equilibrium which results when a little dilute ammonium thiocyanate, NH_4SCN, solution is added to a very dilute solution of ferric chloride, $FeCl_3$. A red colour appears due to the production of ferric thiocyanate, $Fe(SCN)_3$, but the reaction soon comes to equilibrium.

$$3\ NH_4SCN + FeCl_3 \rightleftarrows Fe(SCN)_3 + 3\ NH_4Cl$$

If we now divide the solution into four parts and reserve the

first one for comparison we can show the effect of concentration changes by the intensity of the red colour.

(*i*) Addition of more $FeCl_3$ intensifies the colour. The reaction is driven forward.
(*ii*) Addition of NH_4SCN intensifies the colour. Again the forward reaction is promoted.
(*iii*) Addition of some solid NH_4Cl diminishes the colour. The reverse reaction is promoted but it requires a great deal of ammonium chloride to reverse it enough to be readily noticeable.

The law of mass action enables us to predict the effect of changing the quantities or concentrations present at equilibrium. An increase in the concentration of A will increase the speed of the forward reaction. Since A and B do not react immediately to form C and D, the speed of the reverse reaction will not be increased as much as the speed of the forward reaction. When equilibrium is reached the concentration of B will be less than before and the concentrations of C and D will be increased.

We might make the reaction run forward by decreasing the concentration of either C or D, or both of them. This would decrease the speed of the reverse reaction; then A and B would react until their concentrations decreased far enough to lower the rate of the forward reaction until it again equals the rate of the reverse reaction. This is the basis of chemical control in equilibrium processes. We may state it briefly this way: *A reversible reaction may be made to run toward completion by increasing the concentration of a reactant or reactants, and/or by decreasing the concentration of a resultant or resultants.* This should be known as the *Equilibrium Law* but is often called the Law of Mass Action because it is derived from it.

You will see many applications of this law in later chapters. In the production of synthetic ammonia or sulphur trioxide the product is continually removed from the reaction so as to keep the forward reaction going faster than the reverse reaction.

4. Effect of temperature on equilibrium. The equilibrium point remains apparently constant *only* if the temperature is constant. Since each rate of reaction is affected differently by the temperature the ratio of the forward and reverse reaction rates, which determine the equilibrium point, will be changed by a change in temperature. You will recall that most molecules require an energy of activation before collisions between them can cause reaction. Every reaction has an energy change associated with the chemical alteration. *If the forward reaction is exothermic or heat producing then the reverse reaction must be endothermic or heat absorbing by the same amount.* An exothermic reaction does not need to depend entirely on collisions to secure the energy to activate its molecules; it is producing energy. It therefore is little dependent on a rise in temperature to increase its rate. On the other hand, the reverse reaction uses up the heat of the surroundings and, among other things, depends upon the temperature to maintain its rate. An increase in temperature will increase the rate of the reverse reaction very much but may have little effect on the forward reaction. Such a reaction will have a smaller proportion of resultants at higher temperatures because the reverse or endothermic reaction is accelerated by increased temperature.

It is more direct to simply state that *a reaction which absorbs heat is accelerated and one which gives out heat is inhibited by an increase in temperature.* This is a statement of fact which could be deduced from the Principle of Le Chatelier (see sec. 5).

You should not jump to the conclusion that reactions can be driven to near completion in one direction by changing the temperature. When the temperature is lowered, say 10°C., both the forward and reverse reactions slow down very much, but the endothermic one is retarded much more than the exothermic reaction. Too low a temperature will make many reactions interminably slow. Raising the temperature

may not be feasible for many reasons; the temperature may be inconveniently high for practical purposes, the substances may be unstable, or the nature of the chemical change may be altered. The usual thing is to choose the most suitable temperature which will give the maximum yield (see Fig. 87).

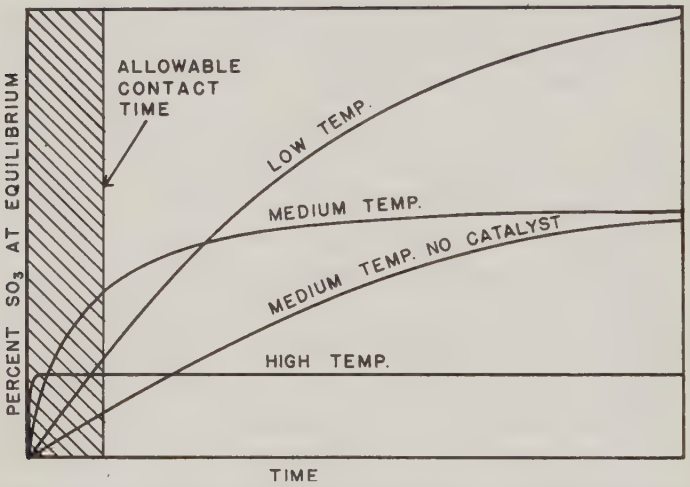


Fig. 87. How the most suitable conditions for an industrial process may be chosen. The effect of the catalyst is shown by the two curves at the same temperature.

5. Le Chatelier's Principle for equilibrium changes. You have seen that it is possible to reason how a change in concentration or temperature will affect the equilibrium point of a reaction. Because pressure changes the concentrations in a gaseous reaction the effect of pressure may also be predicted by the equilibrium law. The effect of factors such as temperature, pressure and concentration may be predicted qualitatively by the Principle of Le Chatelier. *Whenever a stress is placed upon a system in equilibrium it shifts in such a way as to offset or partially annul the effect of the stress.* Now a *system* is any body or set of bodies which the chemist wishes to consider, and a *stress* is any force which he might wish to place upon the system to alter its total energy.

Any chemical reaction in equilibrium is an example of such a system. Consider this reaction:

$$\text{(left) } 4\,HCl + O_2 \underset{r}{\overset{f}{\rightleftharpoons}} 2\,H_2O + 2\,Cl_2 + 28{,}000\text{ cal. (right)}$$

5 volumes **4 volumes**

The forward reaction from left to right is exothermic so the reverse reaction from right to left is endothermic. Let us now deal separately with the three stresses mentioned above.

(1) *Temperature.* Suppose we wish to *raise* the temperature by adding heat energy to the system. It will adjust itself so as to consume heat and offset the effect of the stress. To consume heat it must run from right to left, so the endothermic reaction is promoted. A higher temperature yields a smaller percentage of chlorine and water vapour in the equilibrium mixture. A lower temperature will promote the oxidation of hydrogen chloride.

(2) *Concentration.* Concentration is simpler if considered in terms of the Mass Action Law but it may be thought of as a stress. The reaction will move forward if either hydrogen chloride or oxygen is added, because *the forward reaction consumes* some of the added reactant and partially annuls the effect of its addition. If chlorine is added to increase its concentration the reverse reaction will be accelerated since it uses up chlorine and partly offsets the effect of the added substance.

(3) *Pressure.* The effect of increasing the partial pressure of one constituent is the same as the increase in concentration explained above, but to compress or expand the whole system is difficult to explain by the Mass Action Law. It is much simpler by Le Chatelier's Principle.

Suppose we were to *increase* the pressure on the above reaction system. The equilibrium would shift toward those

substances which occupy the smaller total volume, namely chlorine and water vapour. The reactants, 4 HCl and O_2, occupy five molecular volumes before reaction into 2 H_2O and 2 Cl_2 where they occupy four molecular volumes.

A *reduction* in the total pressure would be offset by the reaction running from right to left. The larger volume occupied by the reactants helps to maintain the original pressure.

Le Chatelier's Principle may be applied to any physical or chemical equilibrium. Let us now look at a few physical equilibria of interest to chemists.

(*a*) *The melting of ice.* Water expands about 1/9 in volume when it changes to the solid state.

$$\text{Water} \rightleftarrows \text{Ice} + 1436 \text{ cal./mol.}$$
$$(18\text{cm.}^3) \rightleftarrows (20.0 \text{ cm.}^3)$$

If pressure is applied to ice it can relieve the pressure by changing into water. This is what happens when you pound fresh snow into a snowball. If the temperature is just at the melting point the pressure of your hand melts the edges of the crystals; when you release the pressure the system opposes the change again by changing to the form which has the larger volume, namely ice, and the crystals are frozen together.

You can readily deduce the effect of temperature on this equilibrium. If you abstract heat in an effort to lower the temperature of water in contact with ice the forward reaction is favoured and some water freezes, liberating 79.91 calories per gram or 1436 calories per mol. The heat of fusion thus keeps the temperature constant unless you convert the liquid into the solid faster than the equilibrium can shift.

(*b*) *The dissolving of a solid.* All particles of matter have an attraction for one another, and if we wish to separate them a short distance from one another as we do in forming a

solution we must exert a force through a distance. This means that we must do work and work takes energy; does it not? Therefore the mechanical process of solution is an endothermic reaction.

$$\text{Solvent} + \text{Solute} \rightleftarrows \text{Solution minus Energy.}$$

For example:

$$\text{Sugar} + \text{Water} \rightleftarrows \text{Sugar Solution minus Energy.}$$

If the temperature is raised the reaction which absorbs heat is favoured so more of the solute dissolves at higher temperatures. If you look at the solubility curves in Chap. 21, sec. 8, you will see that they all curve upward. Calcium hydroxide gives out heat when it is dissolved so its solubility is smaller at higher temperatures. Its solubility curve has a downward trend.

(*c*) *The vapour pressure of liquids.* Vaporization also involves separating the molecules from one another, and it is another process which absorbs energy.

$$\text{Liquid} + \text{Energy} \rightleftarrows \text{Vapour.}$$

For example:

$$\text{Bromine} + \text{Energy} \rightleftarrows \text{Bromine Vapour.}$$

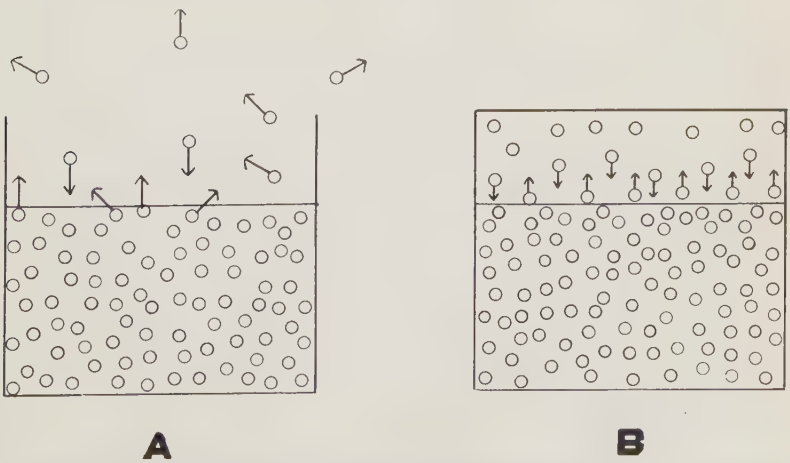


Fig. 88. Vapour pressure equilibrium is attained when the higher energy molecules can return to the surface as fast as they escape.

An increase in temperature will favour the forward reaction so the vapour pressure should be greater at higher temperatures. This is generally true for all substances.

This great Principle of Le Chatelier gives us a means of deducing *how* a change in conditions will affect a system in equilibrium, but it does not enable us to calculate the *magnitude* of the effect.

6. Applications of chemical equilibrium. Although almost all reactions stop somewhat short of completion because an equilibrium is established it is only where the amount of unreacted material is significant that we stop to discuss the detailed conditions which determine the equilibrium point. Many important reactions involving gases reach a dynamic equilibrium. You will find many of them discussed in this topic, e.g., the oxidation of sulphur dioxide to give sulphur trioxide, the union of hydrogen and nitrogen to give ammonia, the combination of nitrogen and oxygen to form nitric oxide, and other equilibria of a similar nature.

The greatest field of application is with solutions of acids, bases, and salts; but we will have to leave this application until we have studied ionization. In Chap. 25 we will devote some time to studying such ionic equilibria as those of weak acids and bases, slightly soluble salts, water and its ions, and many combinations of these. We will also learn how to disturb ionic equilibria by removing substances as gases, as insoluble precipitates or as little ionized compounds.

The principles you have learned about reaction rates and equilibrium will help you to understand a multitude of chemical changes and to predict their probable outcome. If you can do this you are becoming a scientist.

Question Summary

1. (*a*) Ice can be in equilibrium with water at 0°C. Is this a static equilibrium? Explain what is happening.

(*b*) Sugar is dissolved in water to form a saturated solution. Describe the dynamic equilibrium which exists.

2. (*a*) Equal numbers of molecules of chlorine and phosphorous trichloride are kept at constant temperature until equilibrium is attained. Describe the rate changes which occur while equilibrium is being reached.

(*b*) State four characteristics of a chemical equilibrium.

3. (*a*) Describe how the equilibrium point is related to the rates of the forward and reverse reactions.

(*b*) Describe an experiment which shows how the equilibrium point can be shifted by a change in concentration.

(*c*) Write equations for three equilibrium gas reactions. Tell in each case how you could drive the reaction more nearly to completion in the forward direction if the temperature is constant.

4. (*a*) What will be the effect of lowering the temperature on the yield of the forward process in the following:

$$N_2 + O_2 \rightleftarrows 2\ NO - 43{,}200\ \text{cal.}$$

$$2\ SO_2 + O_2 \rightleftarrows 2\ SO_3 + 45{,}200\ \text{cal.}$$

$$H_2S \rightleftarrows H_2 + S - 5{,}260\ \text{cal.}$$

$$PCl_3 + Cl_2 \rightleftarrows PCl_5 + 39{,}500\ \text{cal.}$$

(*b*) Describe how an engineer might decide the best temperature to use in an industrial reaction.

5. (*a*) How does an increase in pressure alter the melting point of ice?

(*b*) Calcium sulphate is deposited as a scale on a steam boiler using hard water. Does it dissolve in water with an evolution or absorption of heat?

(*c*) What is the effect of increasing the pressure on the reactions in Question 4(*a*)? (Assume the sulphur from H_2S is present as a vapour.)

(*d*) Explain why we would expect the vapour pressure of liquids to increase with the temperature.

6. General review of chemical equilibrium:

(*a*) State the meaning of the term chemical equilibrium and illustrate it with an example.

(*b*) Name three factors which may alter the position of the equilibrium point and state a rule about the effect of each of them.

(*c*) How do catalysts affect equilibrium reactions?

(*d*) A mixture of nitrogen and hydrogen will not come to equilibrium over hot concentrated sulphuric acid. Explain.

(*e*) What might be done to promote the forward reactions in the following equilibria:

(*i*) $2\ SO_2 + O_2 \rightleftarrows 2\ SO_3 + 45{,}200$ cal.

(*ii*) $N_2 + 3\ H_2 \rightleftarrows 2\ NH_3 + 24{,}400$ cal.

(*iii*) $4\ NH_3 + 5\ O_2 \rightleftarrows 4\ NO + 6\ H_2O + 214{,}200$ cal.

(*iv*) $C + H_2O \rightleftarrows H_2 + CO$ (at 1000°C.)

(*v*) $CO + H_2O \rightleftarrows CO_2 + H_2$ (at 500°C.)

Chapter 18

Ammonia and Its Compounds

1. Introduction. Ammonia is produced during the decomposition of organic material containing nitrogen, and the odour of ammonia may be noticed in stables because of the decomposition of the manure and urine. Ammonia used to be prepared by the dry distillation of the horns and hoofs of animals, especially those of the hart. The gas obtained by this decomposition was dissolved in water; the solution was known as *spirits of hartshorn*.

Ammonia was known to the ancients and references to it have been found in the writings of Geber. Ammonium chloride was brought from Egypt and was known as *sal ammoniacum*, the name being derived from the Egyptian sun-god Ra Ammon. Ammonium chloride is still known as *sal ammoniac*. In 1727 Hales noticed that when lime was heated with ammonium chloride in a retort the water in a pneumatic trough was drawn up the tube into the retort, but he did not observe the production of a gas. Priestley repeated the experiment using a mercury trough, and collected the gas which he called "alkaline air". The name *ammonia* was given to the gas by Bergman in 1782 and its composition was determined by Berthollet in 1785.

Care must be taken to distinguish between the gas *ammonia*, NH_3, and the *ammonium compounds*, which contain the *ammonium* radical, NH_4.

2. Occurrence. Small quantities of ammonia occur in the air and in some natural waters. Since the gas is formed by the decay of organic material it is found in the soil as the

result of the action of bacteria upon organic matter. The formation of ammonia from decaying material is part of the nitrogen cycle which is shown in Fig. 20. The ammonia produced by decay reacts with organic acids in the humus to form ammonium compounds which can be absorbed by the roots of plants. Some of the ammonia is given off into the air, where it may be converted to nitric acid and returned to the earth in rain water. Ammonium salts are deposited on the sides of some active volcanoes; ammonia is found in the fumaroles of Tuscany.

3. Preparation of ammonia.

A. Laboratory methods.

(1) *By heating a solution of ammonium hydroxide.* Ammonia can be obtained in the laboratory by heating *ammonium hydroxide*, which is a solution of ammonia in water. When the solution is heated the hydroxide is decomposed and the ammonia is driven from the solution, since its solubility is decreased by the rise in temperature.

$$\mathbf{NH_4OH \longrightarrow H_2O + NH_3}$$

(2) *By heating an ammonium salt with an alkali.* The usual method of preparing ammonia in the laboratory is to heat an intimate mixture of slaked lime (calcium hydroxide, $Ca(OH)_2$), and any ammonium salt. Ammonium chloride is generally used. The apparatus is shown in Fig. 89A. Since ammonia is quite soluble in water it cannot be collected in a pneumatic trough and it is collected as shown by the downward displacement of air.

$$\mathbf{2\ NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2\ H_2O + 2\ NH_3}$$

Any base, such as sodium hydroxide, may be used but calcium hydroxide is generally employed because of its cheapness.

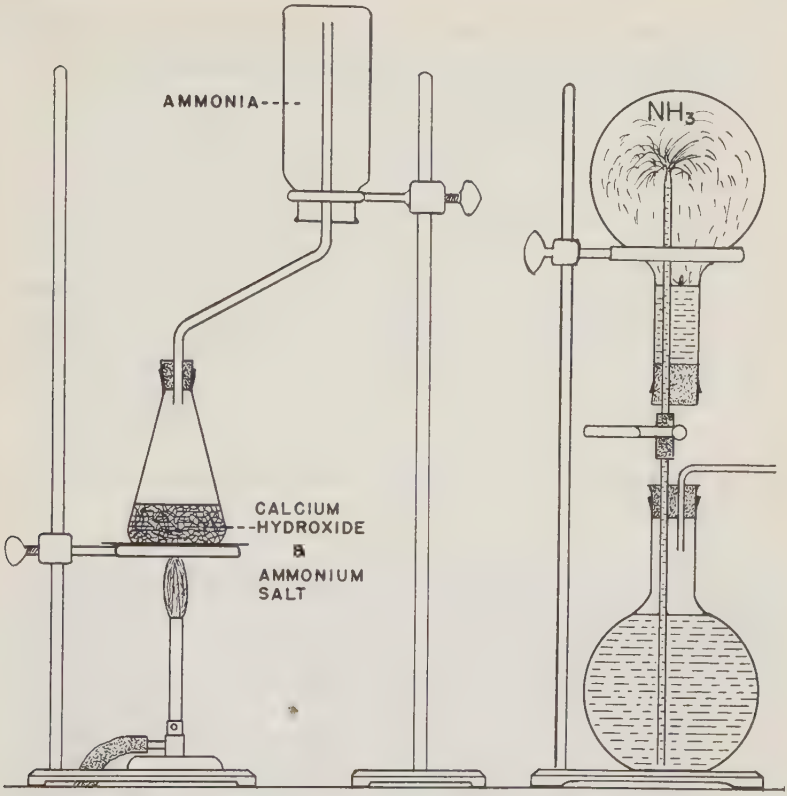


Fig. 89A. Fig. 89B.

Fig. 89A. The preparation of ammonia.
Fig. 89B. Ammonia fountain.

B. Industrial Methods.

(1) *The production of ammonia from coal.* During the dry distillation of coal to produce coke and coal gas some of the nitrogen in the coal is converted to ammonia, which passes off with the coal gas. The coal gas is passed through water in which the ammonia dissolves, giving a solution of ammonium hydroxide and ammonium salts. This solution is treated with slaked lime to convert the salts to ammonium hydroxide and is then heated with steam to drive off the ammonia.

The gas can then be dissolved in water to form ammonium hydroxide, or in sulphuric acid to form ammonium sulphate which is sold for use as a fertilizer.

$$2\ NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

About 20 pounds of ammonium sulphate can be obtained from a ton of coal.

(2) *The Cyanamide process.* Ammonia can be prepared from *calcium cyanamide*, $CaCN_2$, which is made from limestone, coke and nitrogen. It is treated with steam under pressure.

$$CaCN_2 + 3\ H_2O \longrightarrow CaCO_3 + 2\ NH_3$$

Since the nitrogen used to make cyanamide is obtained from the atmosphere, this is a method of *nitrogen fixation.* This term means the conversion of the inert element nitrogen into a form in which it may be used more easily. Before the introduction of the Haber process most of the ammonia used in industry was produced from coal gas and by the cyanamide process.

(3) *The Haber process for producing ammonia.* The Haber process consists of the direct synthesis of ammonia from hydrogen and nitrogen.

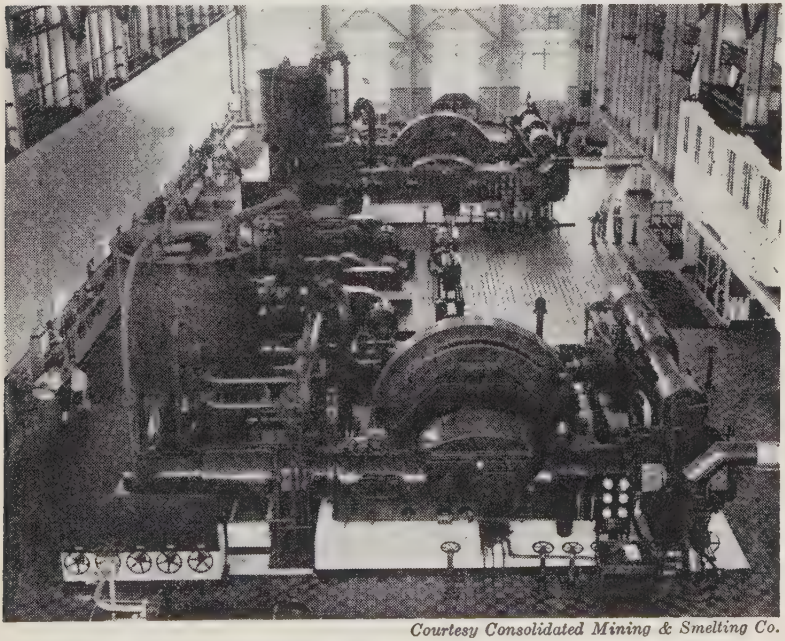
$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3 + 24{,}400 \text{ calories}$$

At low temperatures this reaction proceeds so slowly that it is not of practical value. Since the reaction is exothermic an increase in temperature will tend to drive the reaction towards the left, according to the Principle of Le Chatelier, which will result in the production of smaller amounts of ammonia. The solution of the problem is the use of a catalyst which will allow the reaction to proceed rapidly at a lower temperature. Various substances, among which is a mixture of iron and molybdenum and a mixture of iron oxide and potassium aluminate, have been used with

success. Even with the catalyst the speed of the reaction is too slow unless a temperature of 400°C. to 600°C. is used.

If the volume relations of the equation are studied it is seen that one volume of nitrogen unites with three volumes of hydrogen to form two volumes of ammonia. Four volumes of reacting gas thus gives two volumes of the product. A reaction which decreases in volume as it proceeds will be assisted by an increase in pressure. Accordingly in the Haber process pressures as high as 1000 atmospheres have been used. At these high pressures and temperatures hydrogen will diffuse rapidly through ordinary steels and it has been found necessary to use special alloys for the reaction vessels.

By the use of an efficient catalyst and a high pressure the reaction may be brought to equilibrium rapidly enough to



Courtesy Consolidated Mining & Smelting Co.

Fig. 90. The hydrogen-nitrogen gas mixture for ammonia manufacture is compressed to 3000 pounds per square inch before entering the reactors in this Canadian plant. Why is such a high pressure used?

be commercially useful, while retaining a fairly high proportion of ammonia in the mixture. The ammonia is removed by cooling the mixture, which causes it to liquefy, or by absorbing it in sulphuric or phosphoric acid to make ammonium fertilizers. The removal of ammonia disturbs the equilibrium and the reaction runs continually forward to provide ammonia. The unused nitrogen and hydrogen are returned to the reactor.

The nitrogen used in the Haber process can be obtained from liquid air, and the hydrogen can be obtained from the electrolysis of water or from water gas. By passing a mixture of steam and air through hot coke both nitrogen and hydrogen can be obtained simultaneously. The steam supplies the hydrogen and the air provides the nitrogen. The coke removes the oxygen from both the steam and the air with the production of carbon monoxide. The carbon monoxide must be removed from the mixture of gases since it will poison the catalyst. This is done by passing a mixture of the gas with steam over a heated catalyst, which oxidizes the carbon monoxide to dioxide.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

The Haber process was introduced in Germany shortly before World War I. Since Germany was cut off from a supply of sodium nitrate from Chile by the Allied blockade, she would have had to depend upon the production of ammonia from coal for her supplies of nitric acid, explosives and fertilizers. The Haber process enabled her to wage war for as long as she did. By the time of World War II, almost every country was using this process to obtain their supplies of ammonia and nitric acid. Canada is a leading synthetic ammonia producer with great plants in British Columbia, Alberta and Ontario.

4. The properties of ammonia.

A. *Physical properties.* Ammonia is a colourless gas with a sharp irritating odour. When pure and concentrated it is poisonous but it does not produce a serious effect if it is diluted with air. Its density is a little more than half that of air. Its critical temperature is 132°C. and it is easily liquefied. The liquid boils at −33.3°C. and freezes at −77.7°C. Its heat of vaporization is 327 calories per gram, which is greater than any liquid except water, and the gas is therefore a good substance to use in mechanical refrigerators. Ammonia is very soluble in water. At standard conditions 1 volume of water will dissolve about 1300 volumes of ammonia. The great solubility of ammonia in water is well shown by the *ammonia fountain* which is shown in Fig. 89B.

The apparatus consists of two flasks, one inverted on top of the other, connected by a tube running from the bottom of the lower flask almost to the top of the upper one. This tube ends at the top in a jet and is broken by a piece of rubber tubing which enables it to be clamped by a screw pinchcock between the flasks. The upper flask is filled with ammonia gas. The lower flask, which is provided with a tube for admitting air, is filled with water to which a little sulphuric acid and a few drops of phenolphthalein indicator are added. Since the interior of the upper flask is usually wet the ammonia will dissolve in the water to cause a diminished pressure in the flask. On opening the screw clamp the atmospheric pressure will force the water from the lower flask into the upper one where it will spray through the jet. As soon as some water has entered the upper flask the solution of the ammonia will produce a still more decreased pressure, with the result that the water will continue to flow upward through the jet. The acid will be neutralized and the indicator will turn pink, adding to the effectiveness of the demonstration. If the upper flask is well filled with ammonia it is possible to almost completely fill it with water. At the start of the experiment there may not be sufficient lowering of pressure in the upper flask to cause the water to rise. In that case pressure should be applied to the air tube of the lower flask to force the water up. As soon as some water passes the jet the solution of the ammonia will reduce the pressure immediately.

B. *Chemical properties.* Ammonia does not support combustion and does not burn in air. It will, however, burn in oxygen with a yellow flame, forming water and nitrogen.

$$4\ NH_3 + 3\ O_2 \longrightarrow 6\ H_2O + 2\ N_2$$

If ammonia and air is passed over a hot platinum catalyst, water and nitric oxide are produced. This is an industrial method of making nitric acid (see Chap. 19).

$$4\ NH_3 + 5\ O_2 \longrightarrow 6\ H_2O + 4\ NO$$

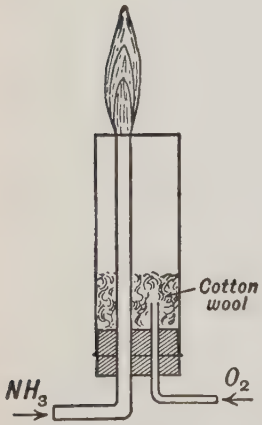


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Fig. 91. Combustion of ammonia in oxygen.

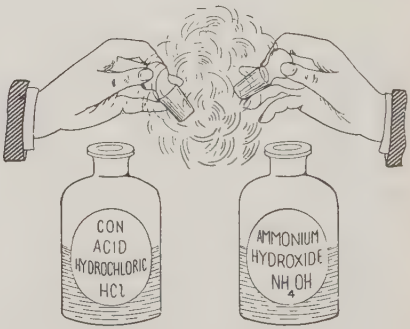

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Fig. 92. Hydrogen chloride and ammonia gas form a white cloud of ammonium chloride.

When ammonia is dissolved in water, it reacts with the water to form the base, ammonium hydroxide.

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

If the solution of ammonium hydroxide is heated this reaction is displaced towards the left and the ammonia is driven from the solution due to the decreased solubility of the gas in the water.

Ammonia will act as a reducing agent with the oxides of some metals. The action of ammonia on heated copper oxide has been mentioned as one of the methods of preparing pure nitrogen (see Chap. 4, sec. 8).

$$3\ CuO + 2\ NH_3 \longrightarrow 3\ Cu + 3\ H_2O + N_2$$

The alkali metals, sodium and potassium, react with ammonia to form an *amide* and liberate hydrogen.

$$2\ Na + 2\ NH_3 \longrightarrow 2\ NaNH_2 + H_2$$

The compound, $NaNH_2$, is known as *sodamide*. Some metals will displace all the hydrogen from ammonia and form nitrides.

$$3\ Mg + 2\ NH_3 \longrightarrow Mg_3N_2 + 3\ H_2$$

Ammonia reacts with acids to give ammonium salts. In the case of hydrogen chloride the ammonium chloride is formed as a finely divided solid which produces a white smoke.

$$NH_3 + HCl \longrightarrow NH_4Cl$$

This reaction acts as a test for ammonia. If a rod is moistened with concentrated hydrochloric acid and placed in ammonia gas a white cloud of solid ammonium chloride will be formed immediately. This reaction is also used as a test for hydrogen chloride. In most cases the characteristic odour of ammonia serves as a useful and sufficient means of identifying the gas.

5. Uses of ammonia. Ammonia is used in the manufacture of nitric acid and ammonium salts. It is also used in the Solvay process for the preparation of sodium carbonate (see Chap. 29, sec. 10). Large quantities of liquid ammonia, known as anhydrous ammonia, are used in commercial refrigerating plants but not in domestic refrigerators. A solution of ammonium hydroxide is sold as *aqua ammonia* or *household ammonia*, familiar to us as a water softener and a cleansing agent.

6. The ammonium salts. A solution of ammonia in water reacts with acids to form compounds known as the *ammonium salts*. In these compounds the NH_4 radical acts like a univalent metallic atom. These salts are prepared by

treating either ammonia or ammonium hydroxide with the required acid.

$$NH_3 + HCl \longrightarrow NH_4Cl$$
$$2\ NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$
$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$
$$2\ NH_4OH + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 2\ H_2O$$

The ammonium salts are all soluble in water and are good electrolytes, although ammonium hydroxide solution is a relatively poor conductor of electricity. They are similar to the salts of sodium and potassium in their chemical reactions but differ in that they are decomposed when heated. Most of them break up into ammonia and the acid but some of them do not give ammonia when heated alone. For this reason the liberation of ammonia when heated is not a test for an ammonium salt. The test is to heat the salt, either dry or in solution, with a base. Under these conditions an ammonium salt will always give off ammonia.

Ammonium chloride, NH_4Cl, known as *sal ammoniac* is a white crystalline solid with a sharp taste. It may be purified by sublimation in a closed system. Some ammonium salts decompose into ammonia and an acid. If this acid happens to be volatile the salt will turn completely into a vapour when heated. When the temperature of the vapour is lowered the gases will recombine to form the salt. This explains the sublimation of ammonium chloride when heated. The salt is used in medicine, in the manufacture of dry cells and in soldering. In soldering, the heat of the iron decomposes the salt and the resulting hydrogen chloride reacts with the oxides of the metals to produce a clean surface on which the solder may run.

Ammonium nitrate, NH_4NO_3, is a white salt which is very soluble in water. The dissolving of this salt in water produces a very low temperature, and mixtures of ammonium

nitrate, water and ice can be used as a freezing mixture. The salt is used in the manufacture of explosives and as a fertilizer. Although it is not considered as an explosive itself, it is dangerous when stored in large quantities; some bad fires and explosions have occurred.

Ammonium carbonate, $(NH_4)_2CO_3$, is a white salt which gives off a noticeable odour of ammonia at ordinary temperatures. When mixed with aromatic oils and alcohol it is used as *smelling salts*.

Question Summary

1. Give a brief account of the history of ammonia.
2. How does ammonia occur in nature?
3. (*a*) Describe the laboratory preparation of ammonia by heating an ammonium salt with an alkali.
   (*b*) Describe the method of obtaining ammonia from coal.
   (*c*) Describe the cyanamide process by an equation.
   (*d*) What is meant by the term nitrogen fixation?
   (*e*) Describe the Haber process for preparing ammonia.
   (*f*) What is the economic importance of the Haber process?
4. (*a*) Give the physical properties of ammonia.
   (*b*) Describe the ammonia fountain demonstration.
   (*c*) Describe the combustion of ammonia.
   (*d*) What is the reaction between ammonia and water?
   (*e*) Describe the reducing action of ammonia.
   (*f*) What is the reaction of ammonia with acids?
   (*g*) What is the test for ammonia?
5. What are the uses of ammonia?
6. (*a*) What are the general properties of the ammonium salts?
   (*b*) What are the properties and uses of ammonium chloride?
   (*c*) What are the properties and uses of ammonium nitrate?
   (*d*) What are the properties and uses of ammonium carbonate?

Chapter **19**

The Oxides and Acids of Nitrogen

THE OXIDES OF NITROGEN

1. Introduction. Nitrogen does not combine directly with oxygen except at very high temperatures and then only in small quantities. There are, however, five oxides of nitrogen:

Nitrous oxide	N_2O
Nitric oxide	NO
Nitrogen dioxide	NO_2
Nitrogen trioxide	N_2O_3
Nitrogen pentoxide	N_2O_5

The first three are well known and may be prepared quite easily. The last two may be prepared but they are of academic interest only.

2. Nitrous oxide. Nitrous oxide, N_2O, was discovered by Priestley in 1772 and was known as "nitrous air". Davy found that when the gas was breathed in small quantities it produced exhilarating and intoxicating effects. For this reason it was called *laughing gas*. It was observed that people were insensible to pain while under the influence of the gas and this observation led to its use as an anesthetic. It was first used as an anesthetic for dental use by Horace Wells in 1844. It is often used as an anesthetic in dentistry and in surgery, in which cases it is mixed with oxygen.

Nitrous oxide may be prepared by heating ammonium nitrate very gently (see Fig. 93). Great care must be taken

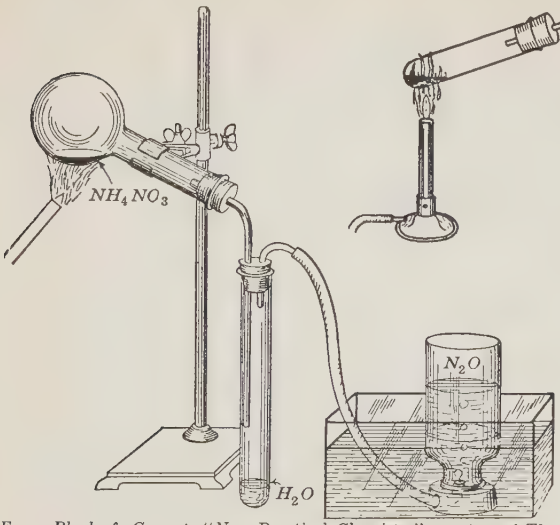

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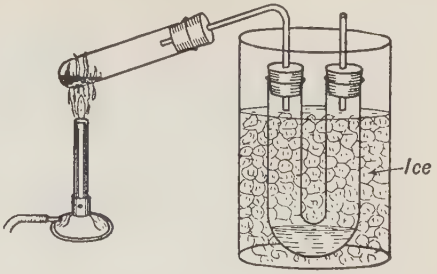
Fig. 93. Laboratory preparation of nitrous oxide.



From Partington: "Inorganic Chemistry", courtesy Macmillan & Company Limited.

Fig. 94. Preparation of nitrogen dioxide from lead nitrate.

in heating this salt as it is liable to decompose explosively.

$$NH_4NO_3 \longrightarrow 2\,H_2O + N_2O$$

The gas is colourless, with a faint odour. It is heavier than air, having the same density as carbon dioxide, and it is fairly soluble in water. Nitrous oxide resembles oxygen in its chemical action. A glowing splinter will burst into flame when placed in the gas, and phosphorus and sulphur burn in it as they do in oxygen. The gas may be distinguished from oxygen in that nitrous oxide will not produce a brown gas when mixed with nitric oxide.

3. Nitric oxide. *Nitric oxide*, NO, was prepared by Mayow in 1669 by treating iron with nitric acid, and Boyle observed that it formed red fumes on contact with air. Priestley is credited with its discovery as an oxide of nitrogen in 1772. Small quantities of the gas are produced in the air during thunderstorms and they form the nitric acid which is present in rain-water.

Nitric oxide may be prepared by the action of nitric acid on copper, which acts as a reducing agent.

$$3\ Cu + 8\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO$$

The gas is colourless and slightly soluble in water. It unites with oxygen at ordinary temperatures to form the brown nitrogen dioxide, NO_2.

$$2\ NO + O_2 \longrightarrow 2\ NO_2$$

4. Nitrogen dioxide. *Nitrogen dioxide*, NO_2, was observed by Boyle in 1671 as a reddish gas which was formed when nitric oxide came into contact with the air. The composition of the gas was determined by Gay-Lussac in 1816. The gas is familiar to most students of chemistry as that which is formed when metals dissolve in concentrated nitric acid; it may be observed during the laboratory preparation of nitric acid.

Nitrogen dioxide may be prepared by treating copper with *concentrated* nitric acid.

$$4\ HNO_3 + Cu \longrightarrow Cu(NO_3)_2 + 2\ H_2O + 2\ NO_2$$

It may also be prepared by heating the nitrate of a heavy metal, such as lead (see Fig. 94).

$$2\ Pb(NO_3)_2 \longrightarrow 2\ PbO + O_2 + 4\ NO_2$$

At low temperatures nitrogen dioxide is a colourless solid which melts at about $-9°C$. As the temperature of the liquid rises it becomes a greenish-yellow colour, which grows deeper until it turns to a reddish-brown and boils at about 26°C., to produce the familiar reddish-brown vapour. As the gas is heated it becomes darker in colour until at 140°C. it is almost black. On cooling, these changes occur in the reverse order. The colour seems to be associated with the vapour density of the substance. At low temperatures the density

is represented by the formula NO_2. At temperatures around 150°C. there is a greater amount of a substance known as *nitrogen tetroxide*, which may be represented by the formula N_2O_4. At intermediate temperatures the gas is a mixture of the two substances. It will be noticed that N_2O_4 is $2(NO_2)$, so that nitrogen tetroxide has a molecular weight which is a multiple of the molecular weight of nitrogen dioxide. Compounds whose molecular weights are multiples of the simplest form of the substance are known as *polymers*.

Nitrogen dioxide is a poisonous gas. It produces headache and sickness if it is present in the air. The gas does not burn and it supports combustion only when the temperature is sufficiently high to cause decomposition of the gas. A most important property of the gas, which is utilized in the preparation of nitric acid, is its action with water. With cold water a mixture of nitric and nitrous acids is produced.

$$2\ NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

With warm water nitric acid and nitric oxide are formed.

$$3\ NO_2 + H_2O \longrightarrow 2\ HNO_3 + NO$$

5. Nitrogen trioxide. *Nitrogen trioxide*, N_2O_3, is the anhydride of nitrous acid.

$$N_2O_3 + H_2O \longrightarrow 2\ HNO_2$$

It may be prepared by cooling a mixture of nitric oxide and nitrogen dioxide to about -21°C. At this temperature it is a blue liquid.

6. Nitrogen pentoxide, N_2O_5, is the anhydride of nitric acid.

$$N_2O_5 + H_2O \longrightarrow 2\ HNO_3$$

It may be prepared by distillation at a low temperature from a mixture of nitric acid and phosphorus pentoxide. The

phosphorus pentoxide is an active dehydrating agent and removes the elements of water from the nitric acid.

$$2\ HNO_3 + P_2O_5 \longrightarrow 2\ HPO_3 + N_2O_5$$

Nitrogen pentoxide is a white solid which melts at 30°C. It unites vigorously with water to form nitric acid.

NITRIC ACID

7. History. *Nitric acid*, HNO_3, was probably known to the ancient Egyptians and it is mentioned in the writings of Geber the alchemist. In 1650 Glauber prepared it by heating nitre with sulphuric acid. Lavoisier showed that it was a compound of oxygen and Cavendish proved that it could be prepared by sparking moist oxygen with nitrogen—the first example of nitrogen fixation. In 1816 Gay-Lussac found that its composition corresponded with the formula HNO_3.

8. Preparation of nitric acid.

A. *Laboratory method.* Nitric acid may be prepared by the general method of preparing a volatile acid from one of its salts. A nitrate may be heated with sulphuric acid which has a much higher boiling point than nitric acid. Sodium nitrate is the most convenient salt to use.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

The lower boiling nitric acid comes off as a vapour and may be condensed in a receiver. The apparatus is shown in Fig. 95. A glass retort is used because nitric acid attacks rubber or cork stoppers. In performing this experiment care must be taken that the vapour of the acid does not come in contact with the skin or the clothing.

B. *Industrial methods.*

(1) *By heating sodium nitrate with sulphuric acid.* The laboratory method of preparing nitric acid from sodium

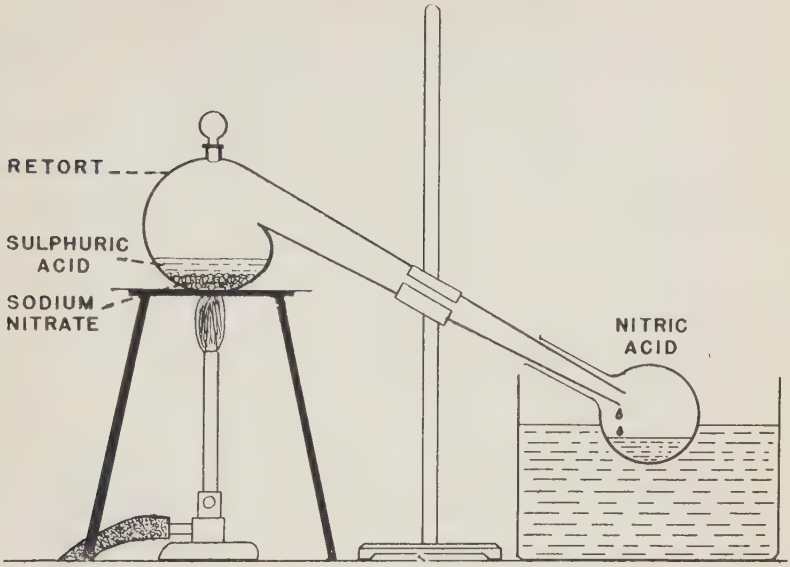


Fig. 95. Preparation of nitric acid from sodium nitrate.

nitrate and sulphuric acid may be used on an industrial scale. In the process by which hydrochloric acid is made (see Chap. 27, sec. 8) this type of reaction is carried to the point where the normal sulphate is produced. This is not done in the case of nitric acid, as the increase in temperature which would be required causes decomposition of the nitric acid. As it is, the nitric acid is distilled under reduced pressure to avoid excess decomposition. The sodium bisulphate produced in this process is known as *nitre cake* and considerable research has been carried out to discover uses for it. It is used in bleaching and dyeing, in the manufacture of textiles, in cleaning and pickling metals, and in the preparation of hydrochloric acid. Until the successful fixation of nitrogen by the cyanamide and other processes all the nitric acid used in the manufacture of explosives, dyes and fertilizers was made from sodium nitrate or obtained from coal gas.

(2) *The Birkeland-Eyde Process.* In 1892 Crookes had shown that air could be oxidized to nitric acid by passing it through an electric arc. In 1902 a scheme of spreading out an electric arc by means of an electro-magnet until it was a disc of flame was devised, and the process of Birkeland and Eyde was established in Norway where there is cheap electric power. This process is now obsolete as it has been supplanted by more economical methods; but it offers a good example of a chemical equilibrium used in an industrial method.

Nitrogen combines with oxygen at a high temperature to form nitric oxide according to the reaction.

$$N_2 + O_2 \rightleftarrows 2\,NO - \text{energy}$$

This is an endothermic reaction; therefore, by the Principle of Le Chatelier, an increase in temperature will drive it towards the right. For collection and use it must be cooled but cooling tends to reverse the reaction and decompose the nitric oxide. To solve this riddle the engineers devised a system of "freezing" the equilibrium by cooling the mixture very suddenly to such a low temperature that the rate of decomposition was immeasurably slow. They did this by directing the hot mixture onto a cold metal plate. An examination of the volumes of the gases on both sides of the equation shows that there is no change in volume in this reaction so a change in pressure will not influence the quantities present at equilibrium.

(3) *The Ostwald Process.* This process depends on the oxidation of ammonia in the presence of a catalyst. Air is filtered and mixed with ammonia, which may be produced by the Haber process (see Chap. 18). The mixture of gases is then passed over a catalyst consisting of platinum gauze as fine as silk heated to a temperature of over 700°C. As the reaction is exothermic sufficient heat is liberated as the reaction proceeds to keep the catalyst at the desired tempera-

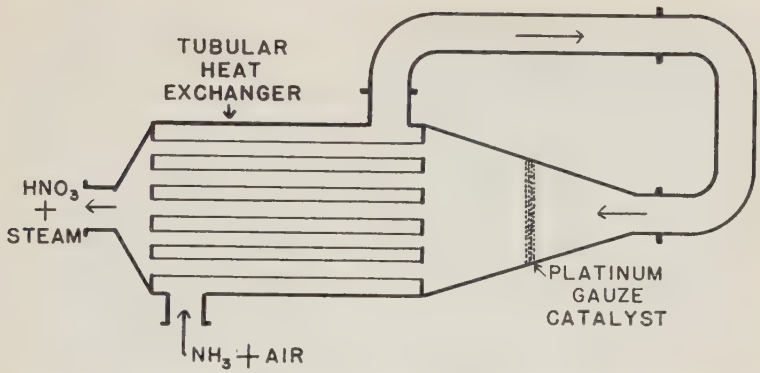


Fig. 96. The Ostwald process for making nitric acid from ammonia.

ture; in fact, as the decomposition of the products is favoured by a high temperature, care must be taken that the temperature does not get too high. As the ammonia and air pass over the catalyst the ammonia is oxidized to nitric oxide.

$$4\ NH_3 + 5\ O_2 \longrightarrow 6\ H_2O + 4\ NO$$

The steam and nitric oxide pass through the pipes of a heat interchanger, the shell of which brings air and ammonia to the catalyst. The incoming gases are heated and the products of the oxidation are cooled. Further cooling is obtained by passing the gases through chrome steel chambers containing pipes carrying cold water. The object is to remove the gases from the presence of the catalyst and cool them rapidly so as to prevent too great a reaction between the products. When cooled the nitric oxide reacts with more oxygen to form nitrogen dioxide, which is led into a tower where it reacts with warm water to give nitric oxide and nitric acid.

$$2\ NO + O_2 \longrightarrow 2\ NO_2$$

$$3\ NO_2 + H_2O \longrightarrow NO + 2\ HNO_3$$

The nitric oxide is returned to the process at the stage where it will become oxidized to nitrogen dioxide. The nitric acid is then concentrated by distillation.

9. Properties of nitric acid.

A. *Physical properties.* Pure nitric acid is a colourless liquid with a freezing point of −42°C., a boiling point of 86°C. and a specific gravity of 1.5. It mixes with water in all proportions and forms a constant boiling solution, boiling at 120.5°C. This constant boiling solution has a specific gravity of 1.4 and contains 68 per cent of nitric acid by weight. A more dilute solution than this will lose water on distillation, and a more concentrated one will lose acid, until the constant boiling mixture remains unchanged. A similar kind of solution is obtained with hydrochloric acid. This constant boiling solution of nitric acid is the "concentrated nitric acid" of the laboratory. This acid will dissolve oxides of nitrogen, especially nitrogen dioxide, and will form a brown liquid which fumes in the air and is known as *fuming nitric acid*. This acid contains about 96 per cent of nitric acid, is less stable than the ordinary concentrated acid and is a more powerful oxidizing agent. The tendency to dissolve oxides of nitrogen, some of which may have been produced by decomposition due to the action of light, causes the ordinary concentrated acid to show a brown colour.

B. *Chemical properties.*

(1) As an oxidizing agent in general. Nitric acid acts as a vigorous oxidizing agent. Carbon, sulphur and phosphorus are oxidized by the acid.

$$C + 4\,HNO_3 \longrightarrow 2\,H_2O + CO_2 + 4\,NO_2$$
$$S + 6\,HNO_3 \longrightarrow 2\,H_2O + H_2SO_4 + 6\,NO_2$$

(2) The action with metals. In its action with metals nitric acid is reduced to its oxides or ammonia, and the metal is oxidized and appears as an oxide or nitrate. The best example of the action with metals is shown by the action with copper. With somewhat diluted acid the following reaction steps may be imagined.

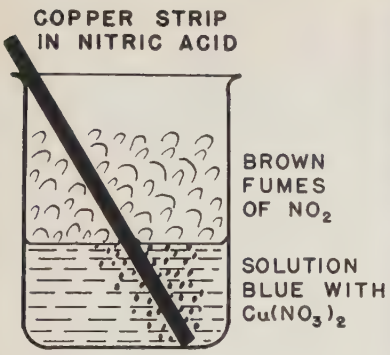


Fig. 97.

Courtesy Eastman Kodak Co.

Fig. 98.

Fig. 97. Metals are oxidized by nitric acid yielding nitrates.
Fig. 98. Pure silver is dissolved in nitric acid to make silver nitrate crystals.

(*i*) In the presence of the copper the nitric acid is reduced to form nitric oxide and oxygen in the atomic state. You will recall that atomic oxygen is known as *nascent oxygen* (see Chap. 5, sec. 9) and is an active oxidizing agent.

$$2\ HNO_3 \longrightarrow 2\ NO + H_2O + 3\ (O)$$

(*ii*) The atomic oxygen acts upon the copper to form cupric oxide.

$$3\ Cu + 3\ (O) \longrightarrow 3\ CuO$$

This equation has been multiplied by three so as to use up all of the oxygen produced by the first equation.

(*iii*) The cupric oxide then reacts with the nitric acid—as does any metallic oxide—and produces cupric nitrate and water, the equation again being multiplied by three.

$$3\ CuO + 6\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 3\ H_2O$$

These three equations may now be added together, the atomic oxygen and cupric oxide cancelled out as being common to both sides, and we get the final equation which

shows the complete reaction, although it is probable that copper is oxidized directly to cupric nitrate.

$$3\ Cu + 8\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO$$

If concentrated acid is used, nitrogen dioxide will be produced. This is either produced directly or as a result of the oxidation of nitric oxide with an excess of nitric acid. The equation is:

$$Cu + 4\ HNO_3 \longrightarrow Cu(NO_3)_2 + 2\ NO_2 + 2\ H_2O$$

With metals more active than zinc, such as magnesium, nitrous oxide, nitrogen, or ammonia are produced. For example:

$$4\ Mg + 10\ HNO_3 \longrightarrow N_2O + 4\ Mg(NO_3)_2 + 5\ H_2O$$

With zinc and very dilute acid, ammonia is produced and the ammonia is neutralized by the nitric acid to form ammonium nitrate.

$$4\ Zn + 10\ HNO_3 \longrightarrow 4\ Zn(NO_3)_2 + 3\ H_2O + NH_4NO_3$$

(3) The action with hydrochloric acid. A mixture of one part of nitric acid and three parts of hydrochloric acid is known as *aqua regia*. This name was used by the alchemists who found that this mixture of acids would dissolve the noble metals such as gold and platinum, which will not dissolve in either acid alone. The dissolving of these metals is probably the result of atomic chlorine which is produced by the oxidation of hydrochloric acid by nitric acid.

$$6\ HCl + 2\ HNO_3 \longrightarrow 2\ NO + 4\ H_2O + 6\ (Cl)$$

When the metals dissolve in aqua regia it is the chloride which is produced (see Chap. 41, sec. 17).

(4) The action with organic compounds. Nitric acid reacts with organic compounds so as to add NO_2 or NO_3 groups to their molecules (see Chap. 44), the process being known

as *nitration*. The action with glycerine produces *nitroglycerine* from which *dynamite* is prepared. From starch or cellulose, *gun-cotton*, *smokeless powder* and *cellulose nitrate* may be obtained. The reaction of nitric acid with the benzene hydrocarbons enables us to synthesize *aniline*, *tri-nitro-phenol* and *tri-nitro-toluol* (T.N.T.).

10. Uses of nitric acid. Nitric acid enables us to introduce nitrogen atoms into organic molecules. This permits their conversion into dyes, by reduction and reaction with other reagents. Many organic compounds containing NO_2 and NO_3 groups are explosives because these groups supply the oxygen to convert the carbon and hydrogen parts of the molecule into gaseous carbon dioxide and water. Nitrates are the best form of nitrogen for plants so ammonium nitrate "prills" or grains are an important fertilizer. Because it is a strong acid and a powerful oxidizing agent it is one of our most important chemicals. Large plants for its production exist in British Columbia, Alberta, Manitoba, Ontario and Quebec.

11. The nitrates. The nitrates are produced by the action of nitric acid upon the metals, oxides, or hydroxides. All nitrates are soluble in water, although some of them such as bismuth nitrate hydrolyze to form slightly soluble basic salts. The nitrates of ammonia, sodium, potassium and calcium are important fertilizers. Ammonium nitrate is used in the manufacture of explosives and under certain conditions the commercial product can decompose with explosive violence.

The test for the nitrates is to add the solution to be tested to some *freshly prepared* ferrous sulphate solution, then to pour concentrated sulphuric acid down the side of the test tube. The heavy acid remains at the bottom of the tube and at the junction of the two liquids acts upon the nitrate, if any is present, to form nitric acid. The nitric acid oxidizes the

ferrous ion to ferric ion and liberates nitric oxide. The nitric oxide reacts with the ferrous sulphate to form the brown substance, $Fe(NO)SO_4$, which forms a brown ring at the junction of the two liquids. Ions which give a coloured product with sulphuric acid will interfere with this test.

SOME OTHER COMPOUNDS CONTAINING NITROGEN

12. Nitrous acid. When sodium nitrate is heated it breaks up into oxygen and sodium nitrite.

$$2\ NaNO_3 \longrightarrow 2\ NaNO_2 + O_2$$

Sodium nitrite is a salt of the hypothetical *nitrous acid*, HNO_2, which cannot be obtained in the free state. If an acid is added to a nitrite, the nitrous acid which is formed decomposes immediately into nitric oxide and nitrogen dioxide.

$$2\ HNO_2 \longrightarrow H_2O + NO + NO_2$$

If a mixture of nitric oxide and nitrogen dioxide is led into sodium hydroxide solution, sodium nitrite is formed. The nitrites are used in the preparation of certain organic compounds and as reagents.

13. Cyanogen, C_2N_2, was discovered by Gay-Lussac in 1815. It is a very poisonous colourless gas with an odour which reminds one of peach kernels. The gas may be prepared by heating mercuric cyanide, a reaction which is analogous to the decomposition of mercuric oxide.

$$Hg(CN)_2 \longrightarrow Hg + C_2N_2$$

14. Hydrocyanic acid, HCN, sometimes known as *prussic acid*, may be prepared by the general method of treating one of the cyanides with sulphuric acid.

$$KCN + H_2SO_4 \longrightarrow NaHSO_4 + HCN$$

The gas, *hydrogen cyanide*, is colourless and quite soluble in water. The solution acts as a weak acid. Both the gas and

the solution are among the most deadly poisons known and the greatest care must be taken in handling the gas or any of the salts of the acid. The gas is used extensively for fumigation and as an insecticide. It should never be used by persons who are not experienced in its use.

The acid is monobasic and forms salts as potassium cyanide, KCN, and sodium cyanide, NaCN. All of these salts are very poisonous. The alkali cyanides dissolve gold and silver, forming double cyanides as $NaAu(CN)_2$ and $NaAg(CN)_2$. The formation of these double salts is the basis of the cyanide process for the extraction of gold and silver from their ores (see Chap. 41).

15. Cyanic acid. If potassium cyanide is heated with an oxidizing agent such as litharge, PbO, *potassium cyanate*, KCNO and lead are formed. The acid, *cyanic acid*, HCNO, decomposes so rapidly into ammonia and carbon dioxide that it cannot be prepared from the cyanates by treatment with an acid. *Ammonium cyanate*, NH_4CNO, is the salt from which Wöhler prepared urea and showed that organic compounds were not necessarily derived from living material (see Chap. 43, sec. 1).

16. Thiocyanic acid. If the alkali cyanides are fused with sulphur, compounds known as the thiocyanates are produced. This reaction is analagous to the oxidation of the cyanides to cyanates, the sulphur taking the place of the oxygen. *Ammonium thiocyanate*, NH_4CNS, gives a blood-red colour with ferric salts.

Question Summary

1. List the names and formulas of the oxides of nitrogen.
2. (*a*) How is nitrous oxide prepared? What are its properties?
   (*b*) What are the uses of nitrous oxide?
3. How is nitric oxide prepared? What are its properties?
4. (*a*) How is nitrogen dioxide prepared?

(*b*) Explain the colour changes when nitrogen dioxide is heated.
(*c*) What are the uses of nitrogen dioxide?

5. What are the properties of nitrogen trioxide?

6. What are the properties of nitrogen pentoxide?

7. Give a brief account of the early history of nitric acid.

8. (*a*) Describe the laboratory method for preparing nitric acid.
(*b*) What are the uses for nitre cake?
(*c*) Describe the arc process for making nitric acid.
(*d*) In the arc process, why must the gas be cooled rapidly?
(*e*) Describe the Ostwald process for making nitric acid.

9. (*a*) Give the physical properties of nitric acid.
(*b*) Describe the action of nitric acid on metals.
(*c*) Describe the action of nitric acid on non-metals.
(*d*) Describe the action of aqua regia in dissolving metals.
(*e*) Describe the action of nitric acid on organic compounds.
(*f*) Name some important compounds produced by the action of nitric acid on organic substances.

10. Give some of the uses of nitric acid.

11. (*a*) What is a test for a nitrate?
(*b*) Give some of the uses of the nitrates.

12. Give the properties of nitrous acid and the nitrites.

13. How is cyanogen prepared? What are its properties?

14. (*a*) How is hydrogen cyanide prepared? What are its properties?
(*b*) What are the properties of the cyanides?

15. What are the properties of the salts of cyanic acid?

16. What are the properties of the thiocyanates?

Chapter **20**

The Oxy-Acids of Sulphur

1. Introduction. The non-metallic element sulphur forms several oxy-acids, two of which are of great importance. Sulphuric acid is of the utmost importance in our industrial life, and it is the most widely used acid. Most of the other acids of sulphur are rather unstable, but their salts are well known and of considerable importance.

SULPHUROUS ACID

2. Properties of sulphurous acid. *Sulphurous acid*, H_2SO_3, is produced by the solution of sulphur dioxide in water (see Chap. 14, sec. 10). As in the case of carbonic acid, any attempt to obtain the free acid results in the liberation of the anhydride. The acid is therefore known only in aqueous solution. Sulphurous acid is dibasic and both the *bisulphites* and *sulphites* are known.

The sulphites decompose on heating to form a sulphate.

$$4\ Na_2SO_3 \longrightarrow 3\ Na_2SO_4 + Na_2S$$

If a bisulphite is heated the normal sulphite is first formed.

$$2\ NaHSO_3 \longrightarrow Na_2SO_3 + H_2O + SO_2$$

The sulphite is then converted to the sulphate. A solution of sulphurous acid readily absorbs oxygen from the air and forms sulphuric acid. Because of the ease with which sulphites are oxidized their solutions always contain traces of sulphate. This oxidation can be retarded by the presence of glycerine or sugar.

The sulphites of sodium and potassium are fairly soluble in water but those of the other metals are not very soluble. The bisulphites, however, are fairly soluble. Sodium sulphite is used in photography. Calcium bisulphite is used in the paper industry, where it is used to dissolve the lignin which binds the fibres of cellulose together.

HYPOSULPHUROUS ACID

3. Properties of hyposulphurous acid. By treating a solution of sulphur dioxide in water with finely divided zinc a zinc salt of *hyposulphurous acid* may be obtained.

$$2\ H_2SO_3 + Zn \longrightarrow ZnS_2O_4 + 2\ H_2O$$

An aqueous solution of the acid may be obtained by treating aqueous solutions of its salts with oxalic acid. The sodium salt has been obtained by the electrolysis of a solution of sodium hydrogen sulphite. On the addition of sodium chloride to the solution *sodium hyposulphite*, $Na_2S_2O_4$, is precipitated.

SULPHURIC ACID

4. Introduction. Sulphuric acid was known to the alchemists and references to it are made in their writings. It was prepared by the distillation of ferrous sulphate and was known as *oil of vitriol*. In 1740 Ward prepared the acid by burning sulphur and nitre in large glass vessels, which were replaced by lead chambers by Roebuck in 1746. The lead chamber process for the manufacture of sulphuric acid formerly supplied all of the world's needs. The contact process allows the preparation of concentrated acid without the necessity of concentrating dilute acid. It also produces a very pure acid but it has not entirely supplanted the older method.

5. The lead chamber process. In this process sulphur dioxide, air and steam are mixed with oxides of nitrogen

and passed into lead chambers where sulphuric acid is formed. During the formation of the sulphuric acid the oxides of nitrogen are set free and are returned to the chambers to be used again. The plant consists of several parts: the *burners*, the *Glover tower*, the *lead chambers* and the *Gay-Lussac tower*. It is shown in Fig. 99.

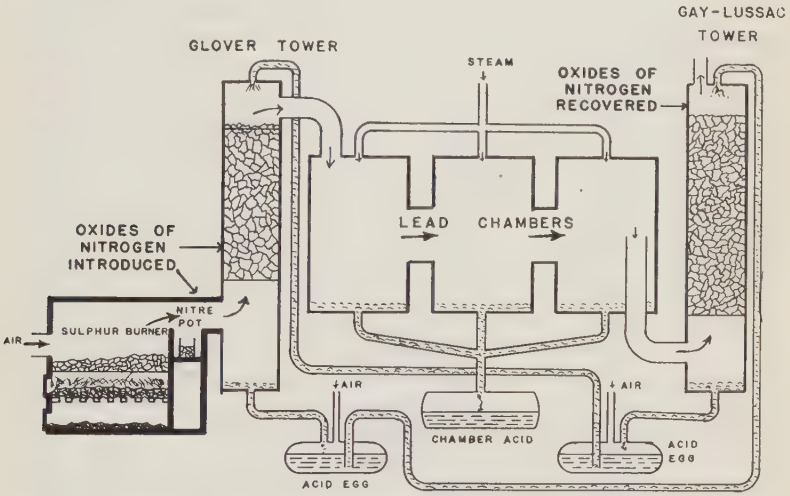


Fig. 99. Diagram of the lead chamber process for making sulphuric acid.

Sulphur dioxide is produced by burning either sulphur or pyrites in a furnace or kiln. The oxygen for this reaction is supplied by an air blast, which also furnishes oxygen for the reactions in the lead chambers. The gases from the burners pass over the *nitre pot* and enter the Glover tower. The nitre pot contains sodium nitrate and sulphuric acid which produce nitric acid. The nitric acid volatilizes, enters the gas stream, and is reduced by the sulphur dioxide to form sulphuric acid and a mixture of nitric oxide and nitrogen dioxide. It is this mixture of nitric oxide and nitrogen dioxide which is known as the *oxides of nitrogen*.

$$2\ HNO_3 + 2\ SO_2 + H_2O \longrightarrow 2\ H_2SO_4 + NO + NO_2$$

Instead of using a nitre pot, the oxides of nitrogen may be produced by the catalytic oxidation of ammonia (see Chap. 19, sec. 8) and introduced directly into the lead chambers. During their passage through the Glover tower the gases pick up a further supply of oxides of nitrogen which have been recovered from the reaction, and pass into the lead chambers. The reactions in the Glover tower by which the recovery of the oxides of nitrogen is effected will be discussed later.

The lead chambers are large rooms lined with sheet lead. They are quite large, being approximately 100×40×40 feet in size, although their dimensions may vary. Anywhere from three to five chambers may be used and the first chamber in the series is usually the largest. In some plants circular towers have been used. The gases from the Glover tower enter the first chamber and pass through all the chambers in series. Low-pressure steam is added through the roof of the chambers. The reactions which take place in the chambers are quite complicated but may be described by the following simplified reactions. The gases unite with the steam to form *nitrosyl sulphuric acid*. This substance is represented by the formula $H(NO)SO_4$ and consists of sulphuric acid in which one of the hydrogen atoms is replaced by the nitrosyl radical, NO.

$$2\ SO_2 + NO + NO_2 + O_2 + H_2O \longrightarrow 2\ H(NO)SO_4$$

If there is a limited amount of water in the chambers the nitrosyl sulphuric acid will collect on the floor in the form of white crystals, which are known as *chamber crystals*. These crystals react with water to produce sulphuric acid and to set free the oxides of nitrogen.

$$2\ H(NO)SO_4 + H_2O \longrightarrow 2\ H_2SO_4 + NO + NO_2$$

The oxides of nitrogen pass into the Gay-Lussac tower and the acid remains on the floor of the chambers. This acid contains from 60 to 70 per cent of sulphuric acid and is known as *chamber acid*. It is impossible to produce a more concentrated acid as it would attack the lead walls of the chambers.

The Gay-Lussac tower was invented in 1827. Its purpose is to recover the oxides of nitrogen which pass from the lead chambers. It consists of a tall tower packed with pieces of tile, coke, or flint, through which concentrated sulphuric acid passes downward to collect in a reservoir at the bottom. The gases from the lead chambers are led in at the bottom of the tower and pass upward through the acid-soaked pieces of inert material. By leading the gases in at the bottom and passing them upward the fresh gas is exposed to the weaker acid, while the fresh acid at the top meets the gases which have already been exposed to the acid and is more able to extract the remaining oxides of nitrogen. This method is known as the *counter-current principle* and is used frequently when gases are to be washed or acted upon by a liquid. The acid reacts with the oxides of nitrogen in the gases and forms nitrosyl sulphuric acid and water.

$$2\ H_2SO_4 + NO + NO_2 \longrightarrow 2\ H(NO)SO_4 + H_2O$$

The dilute nitrosyl sulphuric acid collects in the reservoir in the bottom of the tower and is blown to the top of the Glover tower. In this process the acids are being passed continually from one tower to another. This is done by means of air pressure and avoids the use of pumps which would soon become corroded. The acids flow from the towers into small chambers to which air pressure is applied. These small chambers are known as *acid eggs* because of their oval shape.

The Glover tower was first used in 1859, to assist in the recovery of the oxides of nitrogen. It consists of a tall tower packed with tile or similar

material. This is sprayed by the acid which is pumped from the bottom of the Gay-Lussac tower. The hot gases from the burner pass upwards through the tiles on their way to the lead chambers. The counter-current principle is again applied. Due to the dilution of the acid and the heat of the gases the reaction that took place in the Gay-Lussac tower is reversed, and the water and nitrosyl sulphuric acid form sulphuric acid and oxides of nitrogen.

$$2\,H(NO)SO_4 + H_2O \longrightarrow 2\,H_2SO_4 + NO + NO_2$$

The acid which collects at the bottom of the Gay-Lussac tower has become dilute by contact with excess steam and moist air. When this acid has passed through the Glover tower it has become concentrated, due to the heat and the reaction of the nitrosyl-sulphuric acid with some of the water. This concentrated acid is therefore blown to the top of the Gay-Lussac tower. Theoretically the oxides of nitrogen are absorbed in one reaction and released in another, so that there should be no loss. In practice however, there are unavoidable losses, and an additional supply of these oxides must be introduced continually into the process. The supply of oxides of nitrogen is maintained by the nitre pot or by the direct introduction of the oxides into the lead chambers.

Chamber acid, which is from 60 to 70 per cent sulphuric acid by weight, may be used directly for many purposes, such as the preparation of phosphate fertilizers. In other cases, however, a more concentrated acid is desired. The dilute acid is concentrated in lead pans which may be heated by being placed on top of the sulphur burners. The acid reacts with the lead and produces a protective layer of lead sulphate which prevents further action. When the concentration has been carried to about 77 per cent this protective layer of lead sulphate will be dissolved and the lead will be attacked. The acid can be concentrated to about 94 per cent in vessels made of platinum, iron-silicon alloy, or ceramic material. Chemically pure acid containing 98 per cent of sulphuric acid is prepared by distillation of commercial concentrated acid from glass vessels.

6. The contact process. This process was patented by Philips in 1831, but it was not made a commercial success until about 1901. It consists of the catalytic oxidation of sulphur dioxide to form sulphur trioxide, followed by the

combination of the latter oxide with water to form sulphuric acid. The following equations represent the reactions involved:

$$2\ SO_2 + O_2 \rightleftarrows 2\ SO_3 + 45{,}200\ \text{calories} \quad (1)$$

$$SO_3 + H_2O \rightleftarrows H_2SO_4 \quad (2)$$

It will be observed that the first reaction is driven forward by increased pressure and backward by increased temperature. The oxidation of the sulphur dioxide is very slow and a catalyst must be used. The reaction is exothermic, and a high temperature tends to decompose the sulphur trioxide, according to Le Chatelier's Principle, and so must be avoided. Platinized asbestos was the first catalyst used, but it is easily poisoned, especially by arsenic. Arsenic is apt to be present in sulphur dioxide made from pyrites and the gases must be carefully purified before being passed over the catalyst. Platinized asbestos is prepared by soaking asbestos fibre in chloroplatinic acid and then igniting the mass. The chloroplatinic acid is decomposed on ignition and finely divided platinum remains distributed throughout the asbestos. Calcined magnesium sulphate and silica gel have been used as a support for the finely divided platinum. A platinum catalyst gives a good percentage of conversion to sulphur trioxide if the gases are carefully purified. Ferric oxide and mixtures of vanadium pentoxide with other oxides are more commonly used. These substances are made in tablets with diatomaceous earth as a carrier. They are quite effective, cheaper, and not so liable to poisoning as is platinum.

Pure sulphur is melted in tanks by steam pipes and burned to produce sulphur dioxide. Clean dry air is used to burn the sulphur in modern installations. After passing through a dust remover the air is dried in towers by sulphuric acid, using the counter-current principle. The gases are tested constantly to see if they are free from dust and arsenic, as very slight amounts of impurities will damage the catalyst (see Fig. 100).

The oxidation of sulphur dioxide in the presence of a vanadium pentoxide catalyst is most effective at a temperature of 300°C. to 440°C., since the

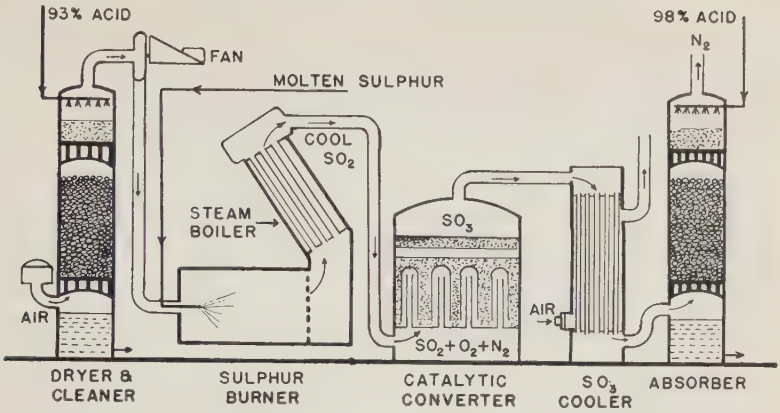
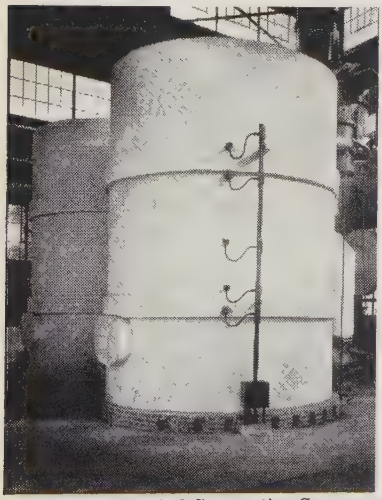


Fig. 100. The contact process for making sulphuric acid.

reaction is exothermic. The incoming hot gases from the sulphur burner are passed through a waste heat boiler where they are cooled by the water pipes which generate steam to run the pumps and fans. During their passage through the first bed of catalyst the gases become heated to about 600°C. at which temperature there is only about 80 per cent conversion into sulphur trioxide. The gases are cooled in a heat interchanger and passed through a second catalyst bed where the reaction is more nearly completed. They pass then to the absorber.



Courtesy Chemical Construction Company

Fig. 101. Contact catalyst towers.

Courtesy Chemical Construction Company

Fig. 102. Absorption towers.

While sulphur trioxide reacts with water to produce sulphuric acid, it cannot be absorbed in water since it forms small droplets which pass through undissolved. It is absorbed in 97-98 per cent sulphuric acid by the counter-current principle in a tower packed with tile or some other suitable material. If the absorption is allowed to proceed to completion, *pyrosulphuric acid*, which is sometimes called *oleum*, or *fuming sulphuric acid*, is produced. The concentration can be regulated by adding water during the absorption so that an acid of any desired concentration can be prepared. This is one advantage which the contact process possesses over the lead chamber method, where the acid has to be concentrated by slow and difficult evaporation. On the other hand, the older method can use sulphur dioxide produced from iron pyrites containing impurities which would poison the catalyst. The contact process produces a purer acid, but the chamber acid is still used extensively for many industrial processes. Canadian manufacture of sulphuric acid is confined mainly to Ontario, Quebec, British Columbia and Nova Scotia.

7. Physical properties of sulphuric acid. Pure anhydrous *hydrogen sulphate* is a colourless, heavy, oily liquid with a specific gravity of 1.83 at 20°C. At low temperatures it forms white crystals which melt at about 10°C. When heated to about 100°C. it decomposes slowly into sulphur trioxide and water, and at about 340°C. it becomes a constant-boiling solution with a concentration of about 98 per cent H_2SO_4. Commercial concentrated sulphuric acid contains from 93 to 95 per cent H_2SO_4 and has a specific gravity of about 1.8.

Sulphuric acid mixes with water in all proportions to form solutions of the acid of varying concentration. A considerable amount of heat is produced when the acid and water are mixed together so great care must be taken when making up solutions of sulphuric acid and the acid must always be

poured into the water. If that is done the heavy acid will settle to the bottom where it will mix gradually with the larger quantity of water. If the water is poured into the acid the drops of water will float on the top of the acid where they may be converted vigorously into steam. This rapid production of steam may cause a spattering of acid from the vessel, with danger from burns or damage to clothing.

8. Chemical properties of sulphuric acid. In aqueous solution, sulphuric acid has the properties of a dibasic acid; it reacts with metallic oxides and hydroxides to form bisulphates and sulphates. Dilute solutions react with the more active metals in the electrochemical series and liberate hydrogen while forming the sulphate of the metal. Very concentrated solutions act less rapidly with metals because the acid properties only develop when water is present. The anhydrous acid can be handled in steel pipes and containers, but the dilute acid must be kept in glass, porcelain, or lead.

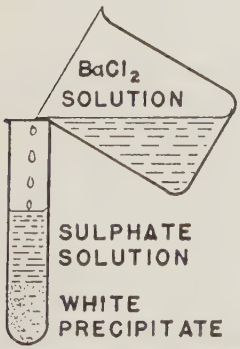


Fig. 103. Test for a sulphate.

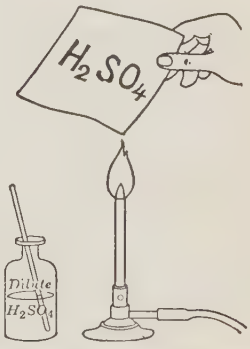


Fig. 104. Sulphuric acid chars paper.

Solutions of the acid or its salts contain the sulphate radical and will give a white precipitate of barium sulphate when barium chloride is added to them. This precipitate does not dissolve in hydrochloric acid.

Concentrated sulphuric acid acts as an oxidizing agent when heated. This is illustrated by the following reactions:

$$C + 2\ H_2SO_4 \longrightarrow CO_2 + 2\ H_2O + 2\ SO_2$$
$$S + 2\ H_2SO_4 \longrightarrow 3\ SO_2 + 2\ H_2O$$
$$Cu + 2\ H_2SO_4 \longrightarrow CuSO_4 + 2\ H_2O + SO_2$$

The concentrated acid will liberate volatile acids from their salts because of the high boiling point of sulphuric acid, 338°C.

The heat produced by the mixing of sulphuric acid and water is due to the formation of hydrates. Because of this ability to combine with water, concentrated sulphuric acid is used as a drying agent for substances which do not react with it. It will even remove the elements of water from chemical compounds. Paper, wood, cotton, sugar and similar substances which contain hydrogen and oxygen are charred by sulphuric acid, since the acid removes the hydrogen and oxygen and leaves the carbon. This is also the cause of the blackening of the skin by the acid. Oleum is a stronger oxidizing, dehydrating, and sulphonating agent than sulphuric acid itself.

Organic compounds can add the SO_3H group from sulphuric acid to their molecules to replace a hydrogen atom. They are then said to be *sulphonated*.

9. Uses. Sulphuric acid is the most extensively used chemical compound which is manufactured by an industrial process. It is said that the extent of the industry of a country may be determined by observing its consumption of the acid. Its use throughout the world amounts to several millions of tons per year. It is used as the cheapest acid to neutralize alkalis and dissolve oxides, as in the refining of petroleum, the pickling of steel, and the absorption of ammonia to make ammonium sulphate fertilizer. Its ability to displace other acids from their salts accounts for its use in the preparation of phosphate fertilizers and nitric acid from nitrates. It can

add sulphur and oxygen to organic molecules, and some of these compounds are our modern sulphonated oils or "soapless" soaps. Sulphonated compounds are the starting point in the manufacture of organic dyes, drugs and other chemicals. Because of its ability to take up water the concentrated acid is widely used as a dehydrating agent for air or other gases if the diluted acid can be concentrated or otherwise utilized.

SOME OTHER OXYGEN ACIDS OF SULPHUR

10. Pyrosulphuric acid. Sulphur trioxide dissolves in concentrated sulphuric acid to give an oily fuming liquid known as *oleum* or *fuming sulphuric acid.* If this liquid is cooled below 0°C. white crystals of *pyrosulphuric* acid, $H_2S_2O_7$, melting at 35°C., are produced. The salts of this acid, the *pyrosulphates*, may be made by heating bisulphates.

$$2\ NaHSO_4 \longrightarrow Na_2S_2O_7 + H_2O$$

Fuming sulphuric acid is used in the manufacture of certain dyes and other organic chemicals.

11. Persulphuric acid. When a mixture of sulphur and oxygen is exposed to a silent electric discharge an oily liquid known as *sulphur heptoxide*, S_2O_7, is produced. This combines with water to form *persulphuric acid*, $H_2S_2O_8$. This acid may be produced by the electrolysis of concentrated sulphuric acid which contains bisulphate ions, HSO_4^-. When these ions are discharged at the anode, they will combine to form persulphuric acid. When solutions of the acid are distilled under reduced pressure, hydrogen peroxide is produced (see Chap. 6, sec. 9).

$$H_2S_2O_8 + 2\ H_2O \longrightarrow 2\ H_2SO_4 + H_2O_2$$

The salts of persulphuric acid, the persulphates, may be obtained by the electrolysis of the solution of a bisulphate. They are vigorous oxidizing agents, since their aqueous solutions decompose to yield oxygen and a bisulphate.

12. Thiosulphuric acid. *Thiosulphuric acid*, $H_2S_2O_3$, is an unstable acid which cannot be obtained in the free state. Its most important salt is *sodium thiosulphate*, $Na_2S_2O_3$, which is used in preparing fixing solution for photographic development (see Chap. 41, sec. 13). It was once thought to be a salt of hyposulphurous acid and was known as sodium hyposulphite. Although it is now known to be a salt of thiosulphuric acid it is still called "hypo" by photographers.

Question Summary

1. What is the most important oxy-acid of sulphur?

2. (*a*) How is sulphurous acid prepared?
   (*b*) What are the properties of the sulphites?

3. What are the properties of hyposulphurous acid?

4. How was sulphuric acid prepared by the alchemists?

5. (*a*) Describe the burners of a lead chamber plant.
   (*b*) What is the function of the nitre pot?
   (*c*) Describe the reactions in the lead chambers.
   (*d*) What are chamber crystals? What is chamber acid?
   (*e*) What are the reactions in the Gay-Lussac tower?
   (*f*) What are the reactions in the Glover tower?
   (*g*) How is the acid moved from one tower to another?
   (*h*) How is concentrated acid prepared from the acid made by the lead chamber process?
   (*i*) Why can dilute sulphuric acid be carried in lead tanks but concentrated acid cannot?

6. (*a*) Describe the contact process for making sulphuric acid.
   (*b*) How may the catalyst become poisoned and what steps are taken to avoid this?
   (*c*) Why are the burner gases cooled before passing through the contact chamber?
   (*d*) Explain the method of preparing sulphuric acid from the sulphur trioxide.
   (*e*) What are the advantages and disadvantages of the contact process as compared with the lead chamber process?

7. (*a*) What are the physical properties of sulphuric acid?
   (*b*) Explain the correct method of preparing dilute solutions of sulphuric acid.

8. (*a*) What is the action of sulphuric acid on metals?

(*b*) What is the action of sulphuric acid on non-metals?
(*c*) Why does sulphuric acid blacken your skin or wood?

9. Give some of the uses for sulphuric acid.

10. What are the properties of oleum?

11. What are the properties of persulphuric acid?

12. What are the properties of thiosulphuric acid?

Topic Four

THE WANDERERS

The apparent disappearance of one substance in another during solution has always been a puzzling phenomenon. When it was discovered that some of these solutions would conduct the mysterious force called electricity while others would not do so, Nature's behaviour was indeed mysterious. The idea of electrically charged particles wandering about in the conducting solutions was soon evolved but the explanation of when and how they are produced depends upon the idea of equilibrium. This explanation made it possible to understand the reactions of acids, bases and salts in solution as well as electrolysis, electrical conductivity and voltaic cells. Systems for making calculations with electrolytes were devised and accurate predictions could be made. A much larger type of wanderer was also discovered to exist in what was known as the colloidal state of matter.

THE PUZZLE OF THE WANDERERS

FARADAY

RAOULT

VAN'T HOFF

VAPOUR PRESSURE LOWERING DUE TO THE NUMBER OF PARTICLES

ACID, BASE & SALT PARTICLES MUST BE CHARGED

TOO MANY PARTICLES IN ELECTROLYTE SOLUTIONS

IONIZATION

CHEMICAL BEHAVIOUR OF ELECTROLYTES

CONDUCTIVITY
ELECTROLYSIS
IONIC MOBILITY
VOLTAIC ACTION

THEORY

1. ELECTROLYTES IONIZE WHEN DISSOLVED IN WATER.
2. IONS AND MOLECULES ARE IN EQUILIBRIUM
3. ANY DEGREE OF IONIZATION MAY BE FOUND.

ARRHENIUS

EXPLANATIONS

IONS ARE ATTRACTED TO ELECTRODES AND DISCHARGED.

METALS AND NON-METALS DIFFER IN TENDENCY TO FORM IONS.

Chapter **21**

Solutions

1. Introduction. You are quite familiar with the idea of a solution. In your study of water you have learned that in the case of the sugar and the water, the sugar is known as the *solute*, the water as the *solvent* and the resulting liquid the *solution*. Solutions play an important part in the study of matter and we shall consider them now in greater detail.

2. The properties of a solution. Potassium permanganate is a violet-black salt which appears usually in the form of very small crystals. If you take a few of these small crystals and place them in a large beaker of water they will sink to the bottom of the beaker and commence to dissolve. The water surrounding them will be coloured purple and streamers of colour will come from them, giving the impression of coloured smoke. If you stir the liquid this colour will be distributed throughout the beaker and the crystals will vanish from sight. From the appearance of the liquid it would seem that the salt has been distributed evenly throughout the liquid; if you take samples from different parts of the beaker you will find that the proportion of the salt in each sample is the same. Therefore you learn that *all parts of a solution are alike*—it is *homogeneous*.

If you weigh the potassium permanganate and the water you will find that you can make up solutions containing different amounts of the salt, but you cannot get more than 6.4 grams to dissolve in 100 grams of water at 20°C. As long as you do not try to exceed this figure of 6.4 grams of salt to 100 grams of water you can make as many different

solutions as you desire. Since solutions do not appear to have definite amounts of solute and solvent and do not follow the Law of Definite Proportions, they must be classed as mixtures and not as compounds. Your experiment with the potassium permanganate and water has shown you that a solution is homogeneous. A solution may be defined as a *homogeneous mixture.*

If you allow the solution of potassium permanganate to stand for a long time there will be still the same depth of colour throughout the liquid. There is no sign of any settling of the particles of the salt to the bottom of the beaker. If any settling took place the colour would become deeper at the bottom of the solution. This fact suggests that the particles of the salt are so small that they are not influenced greatly by gravity but are moving around among the molecules of the water. In fact, they are acting as if they must be molecules themselves. In a true solution the particles of the solute are either molecules or parts of molecules, so that we can say that there is *molecular dispersion.* This is shown diagramatically in Fig. 105A where the particles of solute are shown as solid particles dispersed throughout the molecules of solvent.

3. Suspensions. If you place some sandy loam soil in a tall cylinder of water and stir it you will obtain a cloudy liquid. If this liquid be allowed to stand for a time you find that the particles of sand will settle to the bottom of the beaker leaving the liquid above them cloudy at first, but eventually almost all the particles will settle. If the liquid be stirred you will reproduce the cloudy appearance but again almost all of the particles will settle to the bottom. This mixture of solid and liquid is known as a *suspension.* If you consider the particles of soil as distributed among the molecules of the water it must be obvious that the particles of soil are so large that they are influenced by gravity and thus

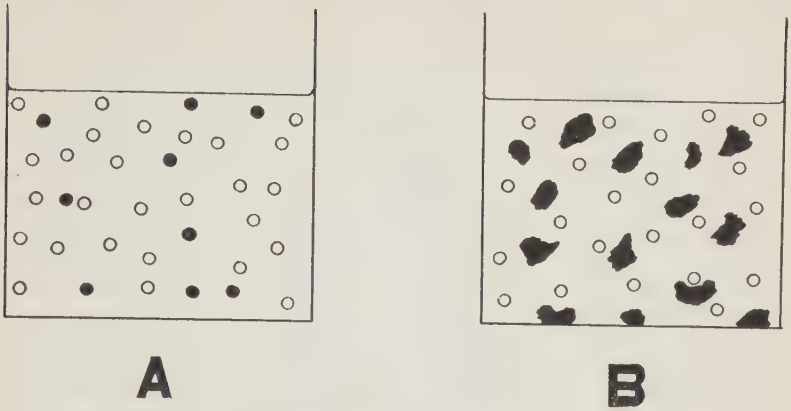


Fig. 105. The dispersed particles in a solution are too small to be distinguished from those of the solvent.

settle to the bottom of the beaker like any other falling object. This is illustrated in Fig. 105B which shows the particles of the solid suspended among the molecules of the water. Since the particles of the solid are not of the same order of magnitude as the molecules, a suspension cannot be considered as a true solution. We thus see that when solution occurs there must be forces of attraction between the molecules of the solute and the solvent which are greater than those holding the molecules of the solute together in the solid shape. The competition between these forces of attraction will thus determine whether a solid is soluble or insoluble in a certain liquid.

4. Types of solutions. There are three states of matter, so if we consider any one state as being dispersed in any one other state there is a possibility of nine types of dispersions. These possibilities are shown in Table 14 together with examples of solutions and dispersions for comparison.

Solutions of solids, liquids and gases in liquids are the most familiar to all of us. To many people the word "solution" means only the dissolving of a solid in water; they are not aware that liquids and gases may be dissolved in liquids.

TABLE 14—TYPES OF SOLUTIONS AND DISPERSIONS

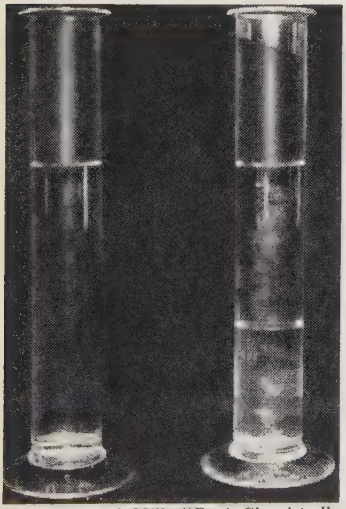
States of Matter	*Solution*	*Dispersion*
1. Solid in Liquid	Solutions of sugar and salts	India ink, muddy water
2. Liquid in Liquid	Glycerine and water, antifreeze	Mayonnaise, milk
3. Gas in Liquid	Soda water, tap water	Whipped cream, meringue
4. Solid in Solid	Metal alloys, brass, solder, etc.	Porcelain, china
5. Liquid in Solid	Mercury amalgams	Cheese
6. Gas in Solid	Hydrogen in metals	Bread and biscuits
7. Solid in Gas	Iodine vapour in air	Smoke
8. Liquid in Gas	Water vapour in air	Fog or mist
9. Gas in Gas	Air	No colloid state possible

The bottle of iodine in the medicine chest is an example of the solution of a solid in a liquid which is not water. Tincture of iodine is a solution of the solid iodine in alcohol. If you add alcohol to water you will find that it will dissolve in all proportions until, when you have more alcohol than water, the water will appear to dissolve in the alcohol and the solute will become the solvent. Liquids that act in this manner are said to be *completely miscible.* If you add ether to water and shake the mixture you will get a cloudy liquid which on standing will separate into two layers. The upper layer consists of a solution of water in ether, while the lower layer consists of a solution of ether in water. These liquids are not completely miscible. Kerosine oil and water after mixing will separate into two layers which consist of water only in the lower layer and oil only in the upper layer. These two liquids are *immiscible.* The familiar drink, soda water, is a solution of the gas carbon dioxide in water (together with various flavourings and sugar). Ordinary tap water contains air in solution as may be shown if some be heated

gently, when the bubbles of the air may be seen escaping from the water.

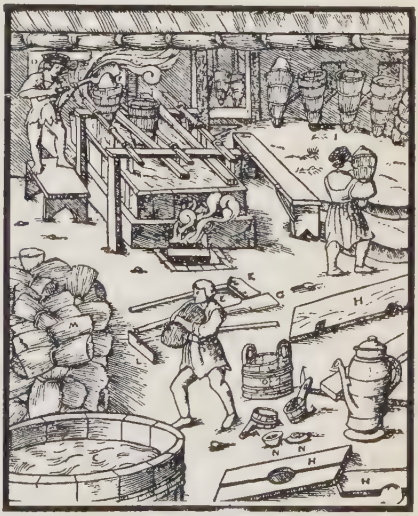
Solutions of solids, liquids and gases, in solids, are not as common as those where a liquid is the dispersing phase. Metallic alloys are good examples of a solid dissolved in a solid. If pieces of gold and lead are pressed together for some time and then examined you will find traces of gold in the lead and traces of lead in the gold. Mercury will dissolve in several metals to form an *amalgam* which is a solid and an example of the solution of a liquid in a solid. The third case, that of a gas dissolved in a solid, is best shown by the solution of hydrogen in platinum or palladium. These metals will take up considerable quantities of the gas, the process being known as *occlusion.*

In the ordinary sense of the word there are no examples of solution taking place in gases. If they do not interact chemically gases will mix together in all proportions. The



From Bayles & Mills: "Basic Chemistry", courtesy The Macmillan Company

Fig. 106. Water and alcohol are miscible but water and oil are immiscible.



Courtesy Canadian Industries Limited

Fig. 107. Separating the solute from the solvent by evaporation in an ancient salt works.

presence of water vapour in the air over liquid water, and iodine vapour in the air over solid iodine, may be considered examples of the solution of a liquid and a solid in a gas.

5. Concentration of solutions. You have seen that the amount of solute in a solution may vary between certain limits so we must find a way of expressing the amount of solute that is present. There is a maximum amount of solute which may be dissolved in a certain solvent. If the amount of solute is close to the maximum amount we say that the solution is *concentrated*. If the amount of solute is far from the maximum we say the solution is *dilute*. These are relative terms. If we examine the solubility, that is, the amount dissolved, of the two salts ammonium nitrate and potassium permanganate, we find that at room temperature, 20°C., you can dissolve 192 grams of ammonium nitrate in 100 grams of water, while in the case of potassium permanganate 6.4 grams will dissolve in the same amount of water. If you prepare a solution of each salt containing 5 grams of the salt in 100 grams of water at 20°C. you will have a concentrated solution of potassium permanganate but a dilute solution of ammonium nitrate, although the amount of each salt is the same in each case. Some people use the terms "weak" and "strong" when referring to concentration but this is not correct as these terms have another meaning which we shall discuss later.

6. Methods of expressing the concentration of solutions. The concentration of solutions may be expressed in physical or chemical units. In physical units we may say that a solution contains so many grams of the solute for every 100 grams or 100 ml. of the solvent. This is very convenient and is used frequently. If we wish to refer to the concentration of a solution in such a manner as to show its ability to react with other substances we use either *normal* or *molar* solutions.

A *normal solution* contains one *gram-equivalent* weight of the solute in one litre of the solution. Note that it is one gram-equivalent weight per litre of *solution* and not of *solvent*. A definite volume of a normal solution of any acid will neutralize the *same* volume of a normal solution of a base. In some cases a normal solution is either beyond the limits of solubility or is too concentrated so we often use a half-normal or deci-normal solution.

A *molar solution* contains one *gram-molecular* weight of the solute in one litre of *solution*. For example: the molecular weight of sodium sulphate is 142.054, so that a molar solution of sodium sulphate will contain 142.054 grams of the salt in a litre of solution. Note that in this case also it is one gram-molecular weight per litre of *solution* and not of *solvent*. The preparation and use of these solutions is discussed more fully in Chap. 24.

7. Saturation. There is a limit to the amount of a solute which can be dissolved in a certain amount of solvent at any temperature and this amount will vary with the character of the solute. You know what happens when we place a piece of solute in a definite volume of solvent as shown in Fig. 86A (see Chap. 17, sec. 1).

A solution which remains constant in concentration while in contact with the undissolved solute is said to be *saturated* at that temperature. If there is not sufficient solute present to produce an equilibrium all of the solute will be dissolved but the solution is *unsaturated*.

The amount of a solute required to produce a saturated solution at a particular temperature is referred to as the *solubility at that temperature*. If we say that the solubility of a salt at 20°C. is 10 grams per 100 g. of solvent we mean that at 20°C. 10 grams of the salt in 100 g. of solvent will produce a saturated solution. If you have less than 10 grams under those conditions the solution will be unsaturated. If you

have more than 10 grams the solution will normally be saturated and the excess will remain undissolved on the bottom of the vessel. A saturated solution will therefore contain all of the solute that it can hold in solution at that particular temperature.

8. The effect of temperature on solubility. In most cases of the solution of solids or liquids in liquids an increase in temperature will increase the solubility (see Chap. 17, sec. 5). Conversely, the solubility will be lowered by a decrease in the temperature. A few substances, such as calcium hydroxide, show the reverse effect, an increase in temperature decreasing the solubility. The effect of temperature on the solubility of some common substances is given in Table 15.

TABLE 15—THE EFFECT OF TEMPERATURE ON SOLUBILITY
(grams per 100 grams of water)

	0°C.	*10°C.*	*20°C.*	*30°C.*	*40°C.*	*50°C.*
Sodium chloride	35.7	35.8	36.0	36.3	36.6	37.0
Potassium permanganate	2.8	4.4	6.4	9.0	12.6	16.9
Potassium nitrate	13.3	20.9	31.6	45.8	63.9	85.5
Ammonium nitrate	118.3	156.4	192.0	241.8	297.0	344.0
Sodium hydroxide	42.0	51.5	109.0	119.0	129.0	145.0
Calcium hydroxide	0.19	0.18	0.17	0.15	0.14	0.13

If the figures representing the solubilities at different temperatures are plotted on a graph and joined by a smooth line a *solubility curve* is obtained. Some solubility curves are shown in Fig. 108.

In the case of solutions of gases in liquids the solubility *decreases* with a rise in the temperature. The presence of air dissolved in tap water may be shown by heating gently a small amount of tap water in a test tube. Bubbles of air appear in the water as the solubility decreases with the increasing temperature. Ammonium hydroxide is a solution

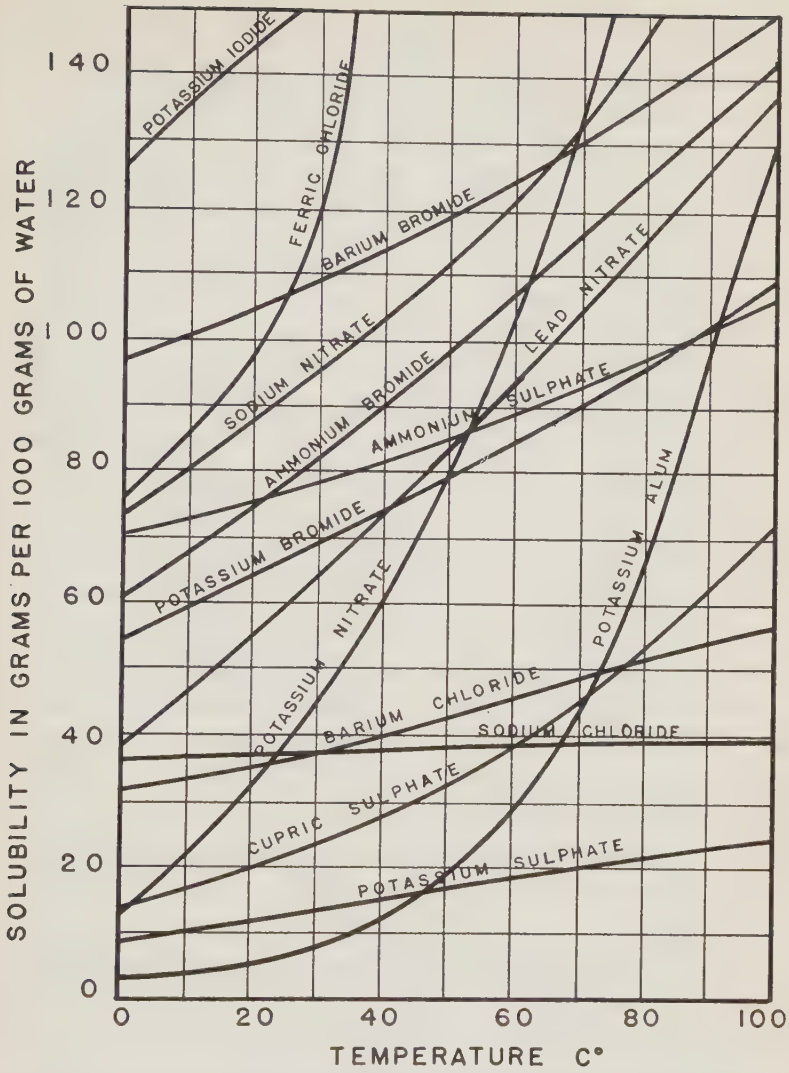


Fig. 108. Increasing the temperature increases the solubility of salts.

of ammonia in water and if it is heated ammonia will be given off. Any gas may be driven more or less completely from solution by boiling. The solubilities of some common gases in water at different temperatures are given in Table 16.

TABLE 16—EFFECT OF TEMPERATURE ON SOLUBILITIES OF GASES

(In grams per 100 grams of water at total pressure = 760 mm.)

Gas	*0°C.*	*10°C.*	*20°C.*	*30°C.*	*40°C.*
Oxygen	.00695	.00537	.00434	.00359	.00308
Hydrogen	.000192	.000174	.000160	.000147	.000138
Nitrogen	.00294	.00231	.00190	.00162	.00139
Carbon dioxide	.3346	.2318	.1688	.1257	.0973
Sulphur dioxide	22.83	16.21	11.28	7.80	5.41

9. The effect of pressure on solubility. Changes in pressure have no appreciable effect on the solubility of any substances except gases. With gases in liquids the solubility is proportional to the pressure of the gas above the liquid. This is known as *Henry's Law* (see Chap. 7, sec. 11).

10. The effect of temperature and surface area on the rate of solution. You know that powdered sugar will dissolve more quickly than the same quantity in a lump. This is because the process of solution requires a contact between the solute and the solvent and must depend upon the amount of surface which the solute presents to the action of the solvent. In this respect the rate of solution is affected in a similar manner as the rate of oxidation (see Chap. 5, sec. 7). An increase in surface of the solute will not affect the *quantity* which may be dissolved in a given amount of solvent but only the *rate* at which it will dissolve.

Since the process of solution depends upon molecular movement anything that will increase the rate of that movement will increase the rate of solubility. Since the molecular velocity is proportional to the temperature an increase in temperature will cause an increase in the *rate* of solution, apart from the change in solubility brought about by the temperature increase.

11. The preparation of saturated solutions. There are three ways by which a saturated solution may be prepared.

By consulting a reference book one can determine how much of the solute will dissolve in a given amount of the solvent at the desired temperature. The correct quantities can then be weighed out, the temperature of the solvent adjusted, and the solute placed in the solvent and well stirred. This method has the disadvantage of requiring accurate weighings and is not usually employed.

Another method is to add a large quantity of the solute to the solvent and to stir the liquid constantly until no more solute appears to dissolve, while there is an excess of solute at the bottom of the vessel. This method is reasonably rapid but there is always a doubt as to whether the equilibrium has been reached between the solute and the solvent so that the solution is saturated.

The most rapid and easy method of preparing a saturated solution is to add the solute to the solvent and heat the solution to boiling while there is an excess of solute on the bottom of the vessel. If the solution is boiling it has reached its maximum temperature which is far above room temperature and one at which there must be a large and rapid dissolving of the solute. The hot solution is then allowed to cool to room temperature. When a hot solution is allowed to cool it will no longer be able to hold in solution as much of the solute as when it was hot. The excess solute will be precipitated to the bottom of the vessel and the solution will always remain in equilibrium with this undissolved solute and will therefore be saturated. If a saturated solution is allowed to cool the excess solute will be deposited on top of the solute with which the solution is in equilibrium. If the temperature is raised more solute will go into solution, if the temperature is lowered more solute will be deposited. If, however, a saturated solution is cooled while there is no solid solute on the bottom of the vessel, the excess solute may not be deposited but may be retained by the solution. In this

case the solution is said to be *supersaturated*. It must be understood that supersaturation must be considered as an accidental occurrence. If it occurs, a sudden jar or the introduction of a small crystal of the solute or even a dust particle will cause immediate precipitation of the excess solute. If there is any solute in contact with the solution supersaturation does not take place.

If a small crystal of the solute is added to a solution a test of the saturation of the solution may be made. If the crystal dissolves the solution is unsaturated; if the crystal does not change the solution is saturated; if the crystal increases in size the solution is supersaturated.

12. Crystallization. When a saturated solution is cooled quickly a large number of small crystals is formed. If the solution is allowed to cool slowly a smaller number of larger crystals is produced. If a saturated solution containing crystals be allowed to stand for some time evaporation will take place and the crystals will increase in size. In fact, when a saturated solution is allowed to stand it will be noticed that small crystals will tend to disappear while larger ones will increase in size. Very large crystals may be obtained if a crystal of the solute is suspended in a saturated solution and allowed to remain for some time. The crystal will tend to increase in size and, with care, very beautiful crystals may be obtained. This may be done easily with a saturated solution of potassium alum or sugar. Rock candy, which is a large crystal of cane sugar, may be made by suspending a string in a saturated sugar solution.

13. Hydrates. If you take a large crystal of cupric sulphate, place it in a test tube and heat it gently, the crystal will turn to a bluish-grey powder and drops of liquid will appear on the cooler parts of the tube. This liquid is water which was chemically combined in the crystal. Water which is chemically combined in a crystal is known as *water of*

hydration. A compound which contains water of hydration is known as a *hydrate*. The number of molecules of water will vary with the substance; this is denoted in the formula by placing a period after the formula of the substance followed by the appropriate number of molecules of water, as: $CuSO_4.5H_2O$; $Na_2CO_3.10H_2O$; $CaSO_4.2H_2O$. It should be remembered that the water of hydration is a part of the molecule and must be included in the molecular weight. It must be pointed out that while most hydrates are crystals not all crystals are hydrates. All hydrates lose their water of hydration when heated and at the same time such crystalline hydrates lose their crystal form. A substance which has lost its water of hydration is said to be *anhydrous*.

Hydrated cupric sulphate $\rightleftharpoons$ Anhydrous cupric sulphate + water vapour

$$\mathbf{CuSO_4.5H_2O \rightleftharpoons CuSO_4 + 5\ H_2O}$$

Every hydrate has a definite water vapour pressure at a given temperature just like water itself, only it is not as large. If the vapour pressure of water around the crystals of hydrated cupric sulphate is greater than this equilibrium vapour pressure no water of hydration is lost, but if the crystals are heated their water vapour pressure may be increased until it exceeds that of the surroundings and the equilibrium will be continually displaced to the right. Anhydrous copper sulphate is not formed in one step but in three steps so there are two lower hydrates, $CuSO_4.3H_2O$ and $CuSO_4.H_2O$; each of these will have a definite vapour pressure at each temperature. In order to secure anhydrous copper sulphate it is necessary to raise the temperature high enough so that the water vapour pressure of $CuSO_4.H_2O$ exceeds that of its surroundings.

14. Efflorescence and deliquescence. If crystals of washing soda, which is hydrated sodium carbonate, $Na_2CO_3.10H_2O$, are allowed to stand on a watch glass exposed to the air they

have such a high water vapour pressure that they will lose their water of hydration at room temperature and become a white powder. Substances which lose their water of hydration on exposure to the air are said to be *efflorescent* and the process is known as *efflorescence*.

Many substances have such low water vapour pressures they will pick up water when exposed to the air to form hydrates. Such substances are said to be *deliquescent* and the property of taking up water from the air is called *deliquescence*. Calcium chloride is a good example of a deliquescent substance. It will take up so much water from the air that it will form a solution. This salt is sometimes spread on roads so that it will take up water and form a cake which prevents the formation of dust.

A great many finely divided inorganic solids such as clay, and some organic ones, attract moisture from the air and a film of moisture condenses upon their surfaces. Such substances are said to be *hygroscopic*. Pure sodium chloride is hygroscopic but it is not deliquescent since it does not form a hydrate. Impure sodium chloride may contain magnesium chloride which does form hydrates and is deliquescent. "Free-running" table salt does not have the magnesium chloride which causes the salt to "pack".

Question Summary

1. Define solvent, solute and solution.

2. (*a*) In the example given of a solution of potassium permanganate explain how it shows the idea of a homogeneous mixture.
(*b*) What facts lead you to believe that you have molecular dispersion in a solution?

3. (*a*) Give some examples of suspensions.
(*b*) What facts lead you to believe that you do not have molecular dispersion in a suspension?

4. (*a*) Try to give examples other than those given in Table 14 of the various types of solutions.
(*b*) Define miscible, amalgam, occlusion.

5. Define a dilute solution, a concentrated solution.

6. (*a*) What is a normal solution?
(*b*) What is a molar solution?

7. (*a*) What is meant by a saturated solution?
(*b*) What is meant by the solubility of a salt at 20°C.?

8. (*a*) What is the effect of temperature on the solubility of solids and liquids in liquids?
(*b*) What is the effect of temperature on the solubility of gases in liquids?

9. What is the effect of pressure on solubility?

10. How is the rate of solution affected by physical changes?

11. (*a*) How might you prepare a saturated solution of a salt?
(*b*) What is meant by a supersaturated solution?
(*c*) If you have a beaker containing a liquid which may be an unsaturated solution, a saturated solution, or a supersaturated solution, how might you tell what it was?

12. (*a*) How would you proceed to obtain very small crystals from a solution?
(*b*) How would you obtain large crystals from a solution?

13. (*a*) What is a hydrate? What is water of hydration?
(*b*) How could you show that a hydrate is a true compound?
(*c*) When do hydrates lose their water of hydration?

14. (*a*) What is meant by efflorescence?
(*b*) What is meant by deliquescence?
(*c*) What is meant by hygroscopic?

Chapter **22**

Solutions and Ionization

1. Introduction. This chapter will try to show you how the study of solutions led men to a far-reaching concept about the nature and behaviour of acids, bases and salts. You will see that many years of work by eminent scientists and many conflicting ideas went into the development of our present-day concepts of ions.

Michael Faraday made a quantitative study of electrolysis and postulated the movement of charged particles in the solutions. These mobile charged particles were called by the Greek name for wanderers, *ions*, but their nature and the manner of their formation was an unsolved problem. Daniell (who developed the cell called by his name), Clausius, Hittorf and several other scientists worked on this problem between 1839 and 1879. The rate of motion of the ions was measured and the manner of their decomposition at the electrodes was deduced from careful observation and measurement. We wish to examine briefly the properties of those solutions which do not conduct the electric current, *non-electrolytes*, and those which do carry a current, *electrolytes*, in order to see how a partial answer was found for this problem of how ions are produced in solutions of electrolytes.

SOLUTIONS OF NON-ELECTROLYTES

2. The lowering of the vapour pressure. In Chap. 15 we saw that the vapour pressure was due to the escape of a definite number of molecules per second from each square

centimetre of a pure liquid surface when the temperature was constant. An equal number returned per second.

If a non-volatile solute is added to the liquid its molecules will be present among the molecules of the liquid and there will be fewer solvent molecules per unit area at the surface. Because of this, fewer molecules of solvent will leave the surface per second, the equilibrium will be established with fewer solvent molecules in the space above the liquid and the vapour pressure will be less. It can be seen that as the number of solute molecules is increased the vapour pressure will be lowered. This leads us to Raoult's Law—*the lowering of the vapour pressure of the solvent is proportional to the number of molecules of the solute present in the solution.* It is important to notice that solutions containing equal numbers of molecules of different solutes in the same quantity of a solvent will have the same vapour pressure. The lowering does not depend on the kind of molecules but only on their number. This is only true if they remain as single particles. The solute should be non-volatile so that its molecules will not interfere with the measurement of the vapour pressure of the solvent.

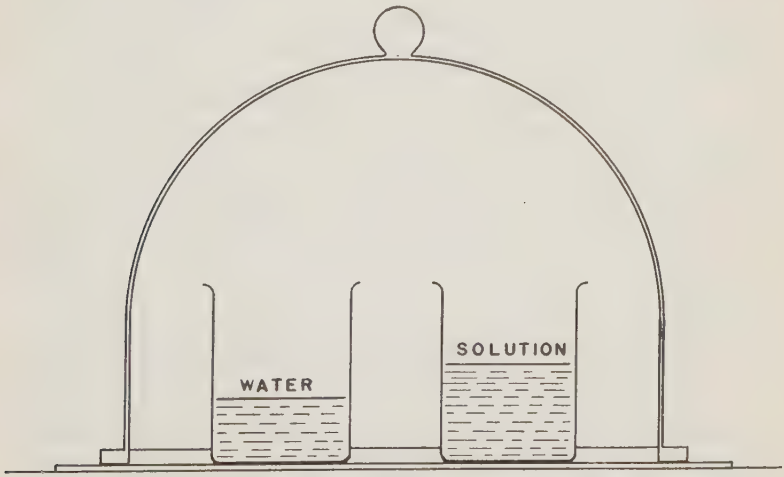


Fig. 109. Pure water has a stronger vapour pressure than a solution so its molecules distil over to dilute the solution.

An interesting example of the lowering of vapour pressure can be shown by considering two vessels placed together under a bell jar as shown in Fig. 109.

One vessel contains pure water while the other contains a solution of sugar in water. Molecules of water escape from both liquids into the space above but the number escaping from the sugar solution is less than the number escaping from the pure water. The water will produce a vapour pressure higher than that which would be in equilibrium with the solution. The solution will therefore receive more molecules than it loses and will increase in volume. If sufficient water is present the process will continue until the solution becomes infinitely dilute.

3. The elevation of the boiling point. Since the presence of molecules of non-volatile solute lowers the vapour pressure of a solution, and the boiling point is the temperature at which the vapour pressure of the liquid becomes equal to the pressure of the atmosphere, it follows that a higher temperature will be required to bring a solution to the boiling point than in the case of a pure solvent. Since the elevation of the boiling point is due to the lowering of the vapour pressure, which in its turn, is due to the number of solute molecules, it follows that the elevation of the boiling point is proportional to the number of solute molecules. Hence *a gram-molecular weight* (6.03×10^{23} *molecules*) *of any non-volatile solute in a given weight of solvent will produce the same elevation of the boiling point.* For example, one gram-molecular weight of cane sugar (342 g.), or of glycerine (92 g.), when dissolved in 1000 g. of water will raise the boiling point from 100°C. to 100.52°C. Solutions of acids, bases and salts, however, will give much greater effects. We called these *electrolytes* because their solutions will conduct a current.

4. The depression of the freezing point. Pure solvents freeze at a definite temperature. The freezing of dilute solutions consists of the crystallization of the pure solvent, during which the molecules of solvent must come together. The presence of the solute molecules hinders crystallization

and freezing will then occur at a lower temperature than that of the pure solvent. Since it is the molecules of solute which cause the depression of the freezing point, the depression must be proportional to the amount of solute that is present. *One gram-molecular weight of any solute should therefore cause the same depression of the freezing point of a given weight of pure solvent.* We find that one gram-molecular weight of cane sugar (342 g.) or of glycerine (92 g.), when dissolved in 1000 g. of water will depress the freezing point by 1.86°C. Again we find that acids, bases and salts produce a greater depression of the freezing point than that produced by substances like sugar and glycerine which are not electrolytes.

The depression of the freezing point of water by a solute is taken advantage of in the use of anti-freeze in the radiators of automobiles. Since the presence of salts would be harmful to the metal in the radiator and engine, either alcohol or ethylene glycol is generally used.

Salt is often thrown on ice to cause it to melt. The salt forms a solution with the surface of the ice and since this solution has a freezing point lower than that of pure water it will remain a liquid. A saturated solution of sodium chloride and ice melts at $-21°$C. so the salt will melt the ice if the ice is above that temperature.

5. Osmosis and osmotic pressure. If we have two liquids, one a pure solvent and the other a solution of a solute in the same solvent, separated from one another by a membrane through which solvent molecules will pass but solute molecules will not, we find that the solvent will pass through the membrane and dilute the solution. A membrane which will allow solvent molecules to pass through but will prevent the passage of molecules of the solute is known as a *semi-permeable membrane*. These membranes may be made by producing a precipitate of cupric ferrocyanide in the walls of a porous jar, or by using bags made from collodion or parchment.

The passage of a solvent through a semi-permeable membrane is known as *osmosis*.

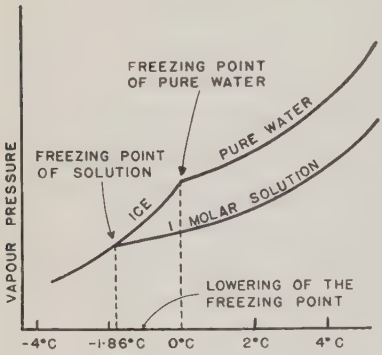


Fig. 110. When the vapour pressure of a solution becomes equal to the vapour pressure of the solid solvent it deposits crystals at a lower temperature than the pure solvent does.

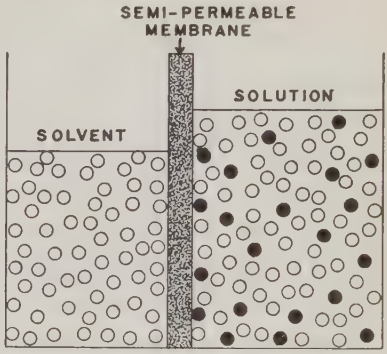


Fig. 111. Osmosis is explained by observing that more solvent molecules strike each square centimetre of the membrane per second from the solvent side than from the solution side.

Let us consider a solvent and a solution of a solute in the same solvent, separated from one another by a semi-permeable membrane as shown in the diagram in Fig. 111. There will be a certain number of molecules on the side of the pure solvent which can pass through the membrane, but on the side of the solution we see that the presence of the solute molecules reduces the number of solvent molecules per unit area which are at the surface of the membrane and thus available to pass through. Therefore more solvent will pass through the membrane towards the solution than will pass through in the opposite direction and the solution will get more dilute. This process will continue until the additional solvent on the solution side of the membrane will build up so much pressure due to the height of the liquid that the passage of more solvent molecules in one direction than another will cease because of the establishment of an equilibrium. The pressure which is required to stop the osmosis may be measured

and is equal to the *osmotic pressure*. Since osmosis, and in turn osmotic pressure, is caused by the molecules of the solute, it follows that *osmotic pressure is proportional to the number of molecules of solute per unit volume*. One gram-molecular weight of any non-electrolyte in one litre of solution will produce the same osmotic pressure, 22.4 atmospheres at 0°C. The osmotic pressure is the same as the pressure would be if the solute were a gas compressed into the same volume as that of the solution.

The osmotic pressure can be measured by an apparatus as shown in the diagram in Fig. 112. A vessel with porous earthenware walls is soaked in a solution of potassium ferrocyanide, rinsed in water, then allowed to stand in a solution of cupric sulphate. The potassium ferrocyanide and the cupric sulphate react together and a precipitate of cupric ferrocyanide is produced within the porous walls of the vessel. The vessel is then filled with a sugar solution, connected to a manometer as shown, and immersed in a vessel contain-

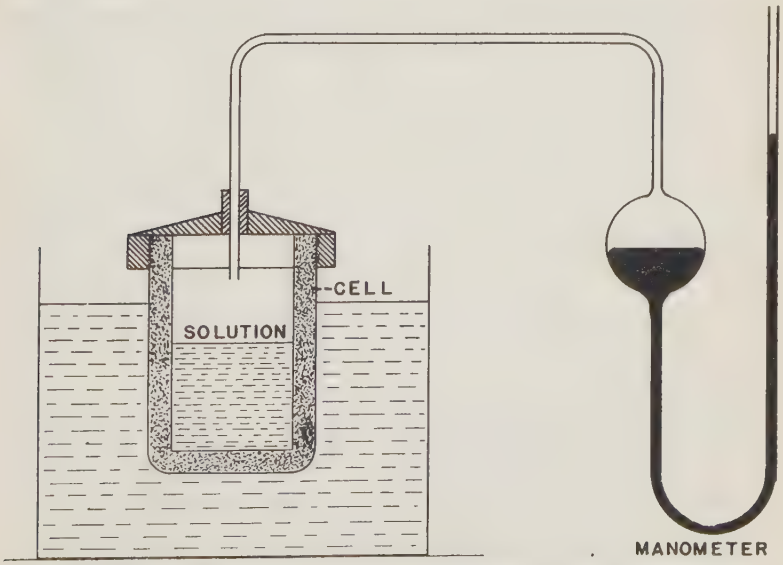


Fig. 112. Diagram of an apparatus for measuring osmotic pressure.

ing pure water. The water will commence to pass through the membrane and the pressure built up in the solution in the porous vessel will be indicated on the manometer.

The phenomenon of osmosis is similar to what takes place when pure water and an aqueous solution are placed together beneath a bell jar as shown in Fig. 109. In that case, the air above the vessels acts as a semi-permeable membrane through which the water can pass and the sugar cannot. Osmosis will also take place when a dilute solution is separated from a more concentrated solution by a semi-permeable membrane. The passage of pure solvent will always be towards the more concentrated solution.

Many substances act as semi-permeable membranes in the life of plants and animals. The membranes lining the cell walls have a selective action with regard to substances passing through them. Water will pass through freely, dissolved salts pass through less freely and complex protein molecules will not pass through at all. The salts and water which pass into the cell form complex compounds which cannot escape and which contribute to the growth of the cell. Solutions which have the same osmotic pressure as that of living cells are known as *isotonic* solutions.

Osmosis plays an important part in the life of plants. A wilted flower will revive if placed in water since the water will pass into the cells and extend them. A plant will wilt when too high a concentration of salts is added to the soil as fertilizer through the removal of water from the plant cells. It is through osmosis that all plants obtain the substances which are necessary for their life.

Many of the processes connected with animal life depend upon osmosis. Blood and the solutions within the cells must be isotonic, otherwise water would be withdrawn from the cells and they would shrink or the water would enter and they would expand. After strenuous exercise too many products

of combustion remain in the muscle cells. These substances take in water by osmosis and expand enough to make you stiff and sore.

6. The determination of molecular weights. We have studied the effects of the number of molecules of a solute on the vapour pressure, the boiling point, the freezing point and the osmotic pressure of a solution. We have learned that, in each case, the same effect is produced by the same number of molecules. Since the gram-molecular weight of any substance contains the same number of molecules we can see that the measurement of these properties of solutions provides us with a method of determining the molecular weight of substances. The measurement of the depression of the freezing point is a convenient method to employ. In aqueous solution one gram-molecular weight of cane sugar dissolved in 1000 grams of water lowers the freezing point of water by 1.86°C. Therefore the weight of another substance that must be dissolved in 1000 grams of water in order to lower the freezing point by 1.86°C. will be the molecular weight.

Suppose we wish to find the molecular weight of a substance X.

We find that 10 g. of X, when dissolved in 100 g. of water freezes at −0.51°C.

Since 10 g. of X in 100 g. of water lowers the freezing point 0.51°C.

100 g. of X in 1000 g. of water will lower the freezing point by 0.51°C.

If 0.51°C. lowering is produced by 100 g. of substance a lowering of 1.86°C. will be produced by $\frac{100 \times 1.86}{0.51}$ or 364.7 g.

Therefore 364.7 is the molecular weight of substance X.

If the substance is not soluble in water we must, of course, use a liquid in which it is soluble. In that event the lowering of the freezing point which is produced by one gram-molecular weight of some substance in that solvent is used instead of the value of 1.86°C., which refers to water only. This method assumes that there is no change in the number of molecules

when the solution is prepared. In an actual solution this condition is realized imperfectly so the result is subject to error; but the method may be used to decide whether the simplest possible chemical formula or some multiple of it is the correct formula. If we wish to know whether the formula of glucose is $C_6H_{12}O_6$ or $C_{12}H_{24}O_{12}$ we find that the molecular weight as given by this method is near 180 and not 360, showing that the simpler formula is correct. The vapour pressure, boiling point and the osmotic pressure may be used similarily in the determination of the molecular weight.

SOLUTIONS OF ELECTROLYTES

7. Electrolytes and non-electrolytes. In 1834 Faraday performed several experiments on the electrical conductivity of solutions and introduced many of the terms that are now in use. Substances such as acids, bases and salts, which conducted electricity, he called *electrolytes*. Substances such as sugar, glycerine and alcohol, which did not conduct electricity, he called *non-electrolytes*. The decomposition of a substance by the passage of an electric current through a solution was called electrolysis. The conductor connecting the solution with the positive pole of the battery was named the positive *electrode* or *anode*, while the other conductor was named the negative *electrode* or *cathode*. The current was supposed to be carried through the solution by small particles called *ions*. These ions (which were not exactly the same as the ones we speak of today) were supposed to be produced in the vicinity of the electrodes and carried the current of electricity through the solution. The negative ones which moved to the anode or positive pole were named *anions* and the positive ones which moved to the negative pole or cathode were called *cations*.

It is important to distinguish this electrolytic conduction from the conduction of electricity by metals. When a solution

of an electrolyte conducts a direct current chemical changes accompany the transfer of electrons, but electrons can flow along a metal conductor in great quantity and produce no other change than a change in temperature.

The migration of coloured ions may be observed by placing a solution of cupric permanganate in the bottom of a U-tube and putting some colourless salt solution above it in each arm of the tube. If a positive electrode is placed in one arm and a negative one in the other it will soon be evident that blue ions are moving towards the negative pole and the violet ions toward the positive pole.

The migration of hydrogen ions, which have the property of acidity, may be seen by placing a gelatine gel which contains phenolphthalein and a trace of sodium hydroxide to make it red, around the electrodes in the U-tube on top of some gelatine gel which has no colour but contains a trace of acid. The red gel around the negative pole will soon lose its colour from the bottom up because of the migration of the positively charged hydrogen ions under the influence of the current. Hittorf devised some ingenious ways of measuring these rates of motion or the mobilities of the ions of various substances before the manner of their production was well understood.

8. The relative conductance of various substances. The current-carrying ability of various substances in solutions of equal concentration may be demonstrated visually by placing them successively in the same conductivity cell. In this cell two electrodes are arranged so as to present a definite area in contact with the solution and to keep a constant distance between the electrodes. A suitable ammeter or an electric light bulb is placed in series with the cell; the two are then connected to a source of current. See Fig. 113. Pure liquids or solutions containing one gram-molecular weight of the solute per litre are then placed in the cell so as to cover

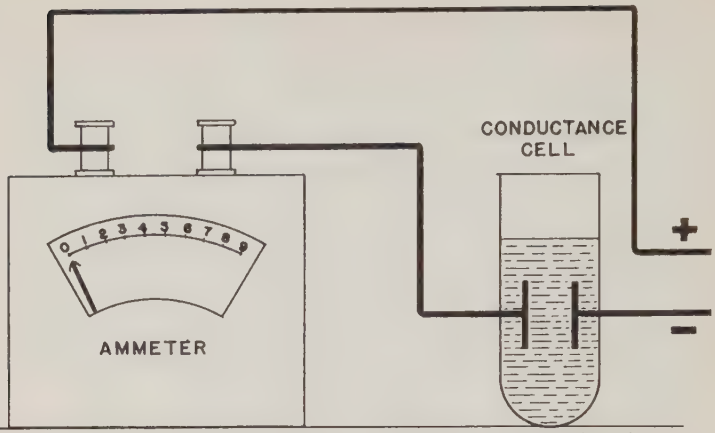


Fig. 113. The relative conductivity of electrolytes can be shown.

the fixed area of the electrodes. The type of results obtained by a careful observer is shown in the following table:

TABLE 17—RELATIVE CONDUCTANCE OF VARIOUS SUBSTANCES

		Conductivity
A.	*Pure Liquid Substances*	
	Distilled water	very slight
	Alcohol	none
	Benzene	none
	Octane	none
	Glycerine	none
B.	*Molar Solutions*	
	Hydrogen chloride in benzene	none
	Sugar in water	none
	Glycerine in water	none
	Alcohol in water	none
C.	*Normal Solutions of Acids, Bases, and Salts, in Water.*	
	Acetic acid	fair
	Formic acid	fair
	Phosphoric acid	good
	Sulphuric acid	excellent
	Nitric acid	excellent
	Hydrochloric acid	excellent
	Ammonium hydroxide	fair
	Sodium hydroxide	excellent
	Potassium hydroxide	excellent
	Lead acetate	poor
	Mercuric chloride	poor
	Magnesium sulphate	good
	Sodium chloride	excellent

Exact measurements make it possible to calculate the conductivity of one equivalent weight of an electrolyte (see Chap. 24) in a given cell. The results of these measurements may be summarized as follows:

(1) Water and non-electrolytes are not good conductors, even in the pure state.
(2) Electrolytes do not behave as conductors unless they are melted or dissolved in solvents such as water.
(3) Some electrolytes are better conductors than others.
(4) The calculated conductivity of one equivalent weight of solute increases with the dilution of the electrolyte.
(5) The conductivity seems to depend on what action the solvent has on the solute.

9. Electrolytes and electrodeposition. Either pure water or pure liquid hydrogen chloride is a poor conductor when used alone, but when a little of the hydrogen chloride is dissolved in the water a current of electricity will be conducted and will *decompose the solution.* This decomposition is the *electrolysis* which accompanies the conduction of a direct current of electricity through an electrolyte which is placed between two inert electrodes. Michael Faraday discovered the exact relations which exist between the amount of current and the quantity of electrolyte which is decomposed at the electrodes. If the decomposition product is a gas it will be evolved; if it is a metal it will be deposited on the electrode as a film of more or less compact material. If the metallic film is adherent and is capable of being polished, the process is called *electroplating.* Electrolysis, electrodeposition and electroplating are different names for the chemical change which is produced at the electrodes by the passage of an electric current.

One *coulomb* is the quantity of electricity which has passed when one ampere has flowed through a conductor for one second. Faraday discovered two simple facts which are called Faraday's Laws of Electrolysis:

(1) The amount of material decomposed is proportional to the amount of current which has passed.

(2) Each equivalent weight of material decomposed requires the same quantity of electricity for its evolution or deposition.

The first law is fairly obvious, i.e., the more current you pass through the solution the more material you will decompose; but the second law has a deep significance. The meaning is shown in Fig. 114.

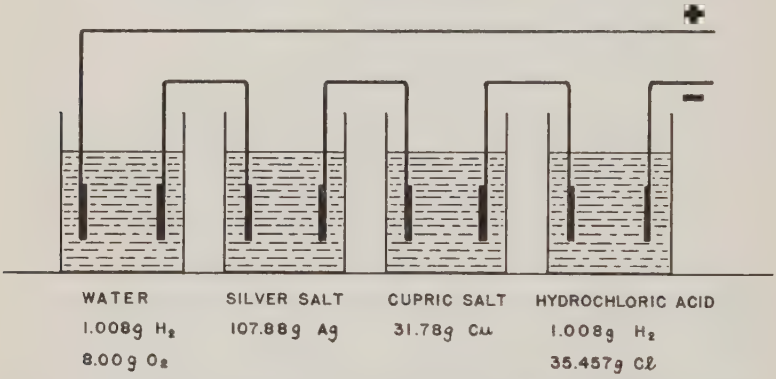


Fig. 114. When one faraday of electricity is passed through a solution it liberates one equivalent weight.

The quantity of electricity which is required to decompose one equivalent weight of a substance is called a *faraday*. It is 96,494 coulombs, or the quantity of electricity which passes when 1 ampere flows through a solution for about 26.8 hours. Thus 1 faraday will liberate 1.008 g. of hydrogen, 8 g. of oxygen, 35.457 g. of chlorine, 107.88 g. of silver, or 31.78 g. of copper from a cupric solution. The quantity of electricity which is required depends upon the change in valence which takes place at the electrodes. Since an equivalent weight is the quantity which has unit valence, this law connects valence directly and simply with the electric charges on the moving particles. When Sir J. J. Thomson and others had

shown that electrons were present in all substances it became evident that the electron was the unit of electricity and that each atom or radical required one or more of these units of electricity for its decomposition or liberation. Each negatively-charged chlorine particle had to lose one electron to become an atom, each silver or hydrogen particle had to gain an electron to become an atom, and so on for all the others. This knowledge was far away when Faraday was performing his experiments.

10. The production of electric current in electrolytes. All these experiments were possible because two different metallic conductors will acquire opposite electric charges when placed in a solution of an electrolyte. This was the discovery of Volta. One metal becomes the negative pole of the voltaic cell; the other conductor becomes the positive pole. If the cell is used the more active metal passes into the form of a salt in the solution, while some other substance is liberated at the positive pole. This action does not take place in non-electrolytic solutions.

The relative activity of metals is most easily measured by measuring the voltage of these voltaic cells. The metal is placed in a 1 molar solution of its salt and connected through a salt bridge, which is a tube full of salty gelatine gel, to a hydrogen electrode to form a cell. A hydrogen electrode is a piece of platinum in a 1 molar acid solution. Hydrogen is bubbled over the platinum which forms an inert metallic conductor. We say the hydrogen electrode in 1 molar acid has a zero potential, so when we measure any other electrode against a hydrogen electrode we find the potential of the metal. The more active a metal is in liberating hydrogen from water or acids the more negative we find its potential to be. Metals such as copper, silver, gold and mercury are found to have positive potentials and we know they do not displace hydrogen from acids. The metals can be arranged in order of their

voltages in what is called an electro-chemical or activity series like that shown in Table 18.

TABLE 18—A SIMPLE ELECTROCHEMICAL OR ACTIVITY SERIES.*

Metals above hydrogen		*Metals below hydrogen*	
Potassium	−2.92	Hydrogen	0.00
Calcium	−2.87	Copper	+0.34
Sodium	−2.71	Silver	+0.80
Magnesium	−2.40	Mercury	+0.80
Aluminum	−1.70	Platinum	+0.86
Zinc	−0.76	Gold	+1.36
Iron	−0.44		
Tin	−0.13		
Lead	−0.12		

*See Chap. 38, sec. 6. for a more complete series.

The metals *above* hydrogen will displace it from acids, while those metals *below* hydrogen will not displace it from acids. The more active metals will displace a less active metal from the solution of one of its salts. This may be shown by putting the steel blade of a knife in some cupric sulphate solution. The iron displaces copper and the blade is plated. It is frequently convenient to remember whether a certain metal is above or below hydrogen in this series as that enables one to predict many of its chemical reactions. It will be noted that the ability to displace hydrogen from acids is only one sign of the activity of a metal. The metals which do not displace hydrogen from acids have activities relative to one another and can therefore be used to displace one another from their salts A familiar trick which boys like to try is that of rubbing copper coins with a little mercuric chloride solution or even a drop of mercury. When the *poisonous* solution is used the copper is coated very quickly since it displaces mercury from its salts.

11. Chemical behaviour of electrolytes. If you add a solution of silver nitrate to a solution of any chloride a pre-

cipitate forms immediately, but if you mix two non-electrolytic solutions it is usually some time before there is any evidence of a reaction. Reactions between molecules of non-electrolytes are generally slow, while reactions involving electrolytes are almost instantaneous. All salts of the same anion or negative radical undergo the same reactions; the same is true for all the salts of the same metal ion or cation. We speak of certain substances as acids because they all have properties which are characteristic of the hydrogen ion. We now attribute the common properties of bases to the hydroxyl ion. All dilute cupric solutions are blue and we conclude that the blue colour is due to the cupric ion. Similarly all permanganates and permanganic acid give violet solutions, all nickel salts give green solutions and all dichromates give orange solutions. These properties indicate that the metal ions and radicals behave independently of one another.

12. Abnormalities in physical properties. We have discussed the effects of the number of molecules of the solute on various physical properties of a solution, such as vapour pressure, freezing point, boiling point and osmotic pressure, and we have mentioned that solutions of acids, bases and salts produce abnormal results. In all cases the effect is much greater than that calculated for the number of molecules which have been added to the pure solvent. For example, one gram-molecular weight of sodium chloride produces almost twice the depression of the freezing point of water that is produced by one gram-molecular weight of sugar. Barium chloride produces nearly three times and ferric chloride gives *over* three times the freezing point depression caused by an equal number of molecules of cane sugar. What is the cause of these abnormalities? Since they take place with electrolytes and not with non-electrolytes it is obvious that there is a connection between these abnormal

physical effects and the mechanism of electrical conductivity in solutions.

The early explanation of conductivity was that the molecules of the solute were dissociated by the influence of the electric potential between the electrodes. This is illustrated in the case of sodium chloride in the diagram shown in Fig. 115. The molecule next to the anode gave up a chlorine atom to be liberated at that electrode, the molecule next in line to the one which had dissociated then passed its chlorine atom on to the first molecule, and so on from molecule to molecule. This explanation was found to be insufficient because the facts learned about the conductivity of solutions showed that the passage of the current and the electric potential which was applied had no connection with the formation of the ions in the solution. All these facts indicated that there must be a considerable number of ions

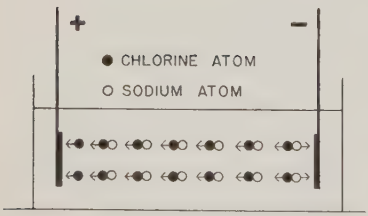
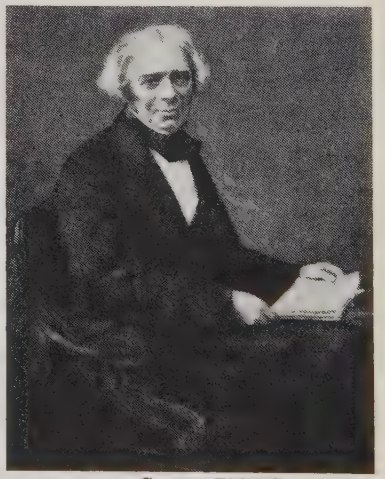


Fig. 115. An erroneous idea about conductivity was that the molecules were dissociated by the charged electrodes.



Courtesy Fisher Scientific Co.

Fig. 116. Michael Faraday (1791-1867), an English chemist and physicist, studied electrolysis and electromagnetic repulsion.

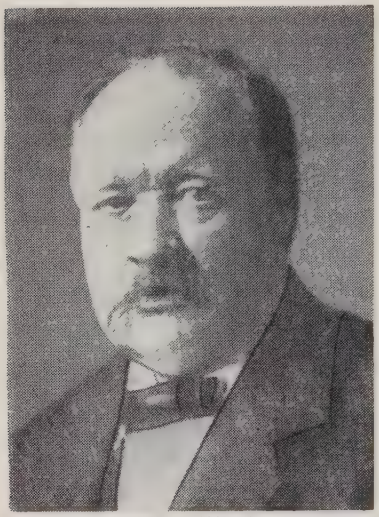
in a solution of an electrolyte *before* the electric potential was applied.

13. The ionization theory of Arrhenius. Svante Arrhenius, a Swedish chemist, reviewed all the above data about (*i*) *conductivity*, (*ii*) *electrolysis*, (*iii*) *ionic mobility*, (*iv*) *chemical behaviour*, (*v*) *voltaic action* and (*vi*) *abnormal physical effects*. He tried to find out where the ions could be produced so as to be responsible for such varied behaviour. In 1887 he presented his famous theory of ionization in a thesis for his doctor's degree. This theory first postulated that *when acids, bases and salts are dissolved in water, their molecules spontaneously dissociate into positively and negatively charged ions.* This theory was not well received at first but it became established finally when it appeared to offer the most consistent explanations for the behaviour of electrolytes. In recent years some modification of this theory has been made, but it does not alter the application of the original theory to weak electrolytes in dilute solution.

The second postulate of the theory is that when an acid, a base or a salt is dissolved in water, only *a certain proportion* of the molecules of the dissolved substance dissociate into ions. In the case of hydrogen cyanide this dissociation will be represented as follows:

$$\mathbf{HCN \rightleftharpoons H^+ + CN^-}$$

These ions will be attracted to one another because of their different electric charges, and they will recombine to form dissolved molecules of hydrogen cyanide, which in turn will break up again into ions. Thus *an equilibrium will be established* which is represented by the double arrows in the above equation. There is always an equal number of positive and negative charges on the ions so the solution will remain electrically neutral.



From Black & Conant: "New Practical Chemistry", courtesy of The Macmillan Company

Fig. 117. Svante August Arrhenius (1859-1927), a Swedish chemist, proposed that the molecules of electrolytes dissociated spontaneously when placed in solution in water.

EXPLANATIONS OF ELECTROLYTE BEHAVIOUR

To be a successful theory these two postulates had to be able to account for all the known effects.

(*i*) *Conductivity.* When a current of electricity is passed through an electrolyte the electricity is carried *by the ions which are already in the solution before the current passes through. The ions are not produced by the current.* The varying conductivities of different solutions thus depend on the degree of dissociation. Substances such as ammonium hydroxide which are not good conductors of electricity apparently do not dissociate to the same extent as do good conductors like sodium chloride.

(*ii*) *Electrolysis.* The positive part of the dissociated substance, the cation, will be drawn to the negative pole or cathode by the electrostatic attraction of the unlike charge. It will be able to take electrons to neutralize its charge and if it is a simple metal ion or a hydrogen ion it will become an atom. Metal atoms will be deposited as films or crystals and hydrogen atoms will combine into molecules of hydrogen and go off as a gas.

The negative part of the dissociated substance, the anion, will be drawn to the positive pole where it can give up its excess electrons to become a neutral atom or undergo chemical reaction into stable products.

The electrolysis of a solution of cupric chloride using platinum electrodes may be taken as an example. One electrode is connected to the negative pole of a battery or other source of direct current. This enables it to receive electrons from the battery or the generator as they are required. The other electrode is connected to the positive wire so that it can dispose of electrons as they are received. The cupric ion is able to form a neutral unit with two univalent chloride ions so it must be divalent or have a positive charge of two units. It is written Cu^{++} to show it has given up two electrons—one to each chlorine atom which is written Cl^-.

$$CuCl_2 \longrightarrow Cu^{++} + 2\ Cl^-$$

The positive Cu^{++} ions near the negative electrode are attracted to it where they receive electrons to become Cu atoms. They will then deposit themselves on the electrode as free metal. More Cu^{++} ions will diffuse toward the surface of the electrode to restore the concentration.

Negative chloride ions will be attracted to the nearby positive pole or anode, where if sufficiently numerous they will give up electrons to become chlorine atoms. The chlorine atoms will unite to form chlorine molecules which will eventually pass off as a gas.

If the anode is made of copper the chlorine atoms can then attack the copper to reform copper chloride. The process of depositing copper on the cathode and dissolving it from the anode can then continue indefinitely, as long as the proper conditions are provided. Such a process of electrolysis where the electrolyte is regenerated and the substance is continually deposited is known as *electrodeposition or electroplating*.

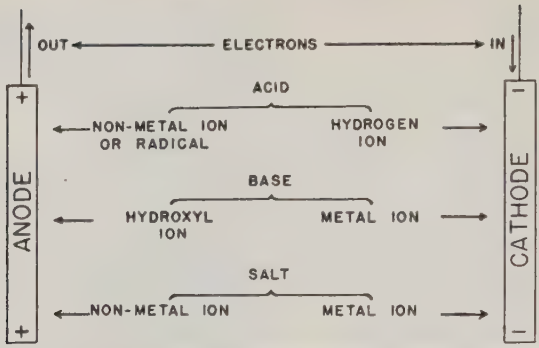


Fig. 118. Acids, bases and salts form ions when placed in water and the anions migrate toward the positive plate while the cations go toward the negative plate.

The electrolysis of water is a familiar experiment. A little sulphuric acid is added to make the liquid an electrolyte. Hydrogen ions are attracted to the negative pole to be discharged and the hydrogen atoms unite to form molecules which are evolved as a gas. The production of the oxygen at the anode is often wrongly explained. We should note that water itself produces both hydrogen and hydroxyl ions, so in addition to the sulphate ions from the sulphuric acid, which are very difficult to discharge, OH^- ions are also present. These OH^- ions are discharged more easily than sulphate ions at the anode to form oxygen and water.

$$4\ OH \longrightarrow 2\ H_2O + O_2$$

More hydrogen and hydroxyl ions are furnished by the further dissociation of the water as they are removed by the electrolysis so the acid is really present to improve the conductivity of the solution.

Electrolysis always accompanies the conduction of direct current through a solution as the process just described continually removes electrons from the cathode and supplies electrons to the anode. This means that electrons are transferred across the solution when some substance in solution is

decomposed in the process. Faraday's Laws are thus explained by the ionization theory. The more current that is passed the more material must be decomposed. This is the first law. The second law is equally simple. It takes one electron to carry one hydrogen atom, one sodium atom, one silver atom, or one of any univalent atom to the electrode to be decomposed. One faraday of electricity is 6.03×10^{23} electrons so it will cause the decomposition of 1.008 g. of hydrogen, 22.997 g. of sodium, or 107.88 g. of silver. It will be observed that these are the equivalent weights of these elements. The same quantity of electricity will only transfer 3.015×10^{23} Cu^{++} ions to the cathode because they require two electrons apiece for their deposition. These will only have one-half of the gram atomic weight of copper because the gram atomic weight is the weight of 6.03×10^{23} atoms of copper. The equivalent weight of copper as cupric ions is one-half of the atomic weight so for a divalent ion the faraday of electricity decomposes one equivalent weight. The same is true regardless of the charge on the ion. This is Faraday's second law.

(*iii*) *Ionic mobility.* The reason for the migration of the blue ions of cupric permanganate to the negative pole and the violet ones to the positive pole could now be understood.

$$\underset{}{Cu(MnO_4)_2} \longrightarrow \underset{\text{(blue)}}{Cu^{++}} + 2\ \underset{\text{(violet)}}{MnO_4^-}$$

The blue ions were positive cupric ions and the violet ones were negative permanganate ions. How would you predict that they would migrate?

(*iv*) *Chemical behaviour.* The reason for the instantaneous nature of ionic reactions now became clear. Each electrolyte exists as charged ions in solution and when they are mixed the ions can attract one another and recombine in a new manner. If the new combination does not dissociate

readily the process is not spontaneously reversible and a permanent conversion has occurred. This is discussed more fully in the next chapter.

(*v*) *Voltaic action.* It was evident that atoms on the surface of metals could become ions if they could transfer away the required number of electrons. They could then repel their similarly charged fellows and go away in solution. The more active metals could do this more readily and thus they would acquire the largest negative charge. When any two different metals were placed in an electrolyte the more active one would become the negative pole of a voltaic cell and the less active metal or carbon would make the positive pole.

(*vi*) *Abnormal physical effects.* The explanation of the abnormally large effects on the lowering of the vapour pressure and the freezing point, the elevation of the boiling point, and the greater osmotic pressure of electrolytes has already been indicated but a few specific examples may be given to make it clearer.

Since sodium chloride is a good conductor it would be expected that almost all of the salt would produce ions in solution; so that, for each molecule of the undissolved salt, you would have *two ions* instead of *one dissolved molecule.* This would mean that there would be twice as many particles in the solution than if the substance did not dissociate. In the case of sugar, alcohol, glycerine, etc., since these substances are not acids, bases or salts, there will be no dissociation and there will be as many molecules of the dissolved substance as there were molecules of the substance present. This will explain the apparently abnormal results obtained in the measurement of certain physical properties of electrolytes when compared to non-electrolytes. You will remember that these physical properties of solutions are due to the *number* of particles of the solute, so that if you have twice the effect you will expect to have twice as many particles.

In the case of barium chloride the molecule consists of one barium atom and two chlorine atoms. The effect of this salt on the measurement of the physical properties of its solution is to produce approximately *three* times the effect produced by an undissociated substance. It would thus appear that barium chloride dissociates so as to produce three ions, and there would be one barium ion and two chloride ions. Since the solution is electrically neutral there must be as many positive charges as there are negative charges, and the barium ion must carry two positive charges in order to balance the effect of the negative charges on the two chloride ions. As the valence of chlorine is 1 while that of barium is 2 we see that *the number of charges on an ion is equal to the valence of the atom or radical from which the ion is produced.* Barium chloride will thus dissociate as follows:

$$BaCl_2 \rightleftarrows Ba^{++} + Cl^- + Cl^-$$

which can be written more simply as,

$$BaCl_2 \rightleftarrows Ba^{++} + 2\ Cl^-$$

Similar considerations applied to ferric chloride suggest that it dissociates as follows:

$$FeCl_3 \rightleftarrows Fe^{+++} + 3\ Cl^-$$

In the case of ammonium sulphate, a substance composed of two radicals, the dissociation would be expressed as follows:

$$(NH_4)_2SO_4 \rightleftarrows 2\ NH^+_4 + SO_4^{--}$$

We see that an ion is therefore an atom or a radical with an electric charge and that *every atom or radical will produce one ion* on dissociation, although the number of charges on each ion will vary with the valence of the atom or radical.

Question Summary

1. Outline briefly the progress which had been made in the study of solutions of acids, bases and salts.

2. (*a*) Explain the evaporation of a liquid which is allowed to stand in the air.

(*b*) How does evaporation cool a liquid?

(*c*) Explain how evaporation may be used to keep liquids cool in tropical countries.

(*d*) Explain the existence of vapour pressure.

(*e*) How does a rise in temperature produce an increase in vapour pressure?

(*f*) What is Raoult's Law?

(*g*) If a beaker containing water is placed under a bell jar with a beaker containing a salt solution, explain why the water will leave the beaker and move to the beaker containing the solution.

3. Explain the elevation of the boiling point of water if a solute be dissolved in it.

4. Explain the depression of the freezing point of a liquid if a solute be dissolved in it.

5. (*a*) What is a semi-permeable membrane?

(*b*) How might you construct a semi-permeable membrane?

(*c*) Explain the occurrence of osmosis.

(*d*) How can osmotic pressure be measured?

(*e*) What is the relation between osmotic pressure and the molecular weight?

(*f*) Explain how osmosis is like the phenomenon which takes place in the experiment described in Question 2 (*g*).

(*g*) What is meant by an isotonic solution?

(*h*) Discuss the role of osmosis in the life of animals and plants.

6. (*a*) How could you use the elevation of the boiling point of a solvent to determine the molecular weight of a substance which is soluble in that solvent?

(*b*) How could osmotic pressures be used to determine the molecular weight of a substance?

7. Explain the meaning of the following terms: electrolyte, non-electrolyte, electrolysis, electrode, anode, cathode, ion.

8. (*a*) How would you demonstrate that a hydrochloric acid solution is a better conductor than an acetic acid solution of the same concentration?

(*b*) What conclusions can be drawn from the table of relative conductances in this chapter?

9. (*a*) State Faraday's Laws of Electrolysis.

(*b*) If you knew the charge representing the unit of electricity, describe how you would calculate the number of atoms in one gram atom.

10. (*a*) How would you make a voltaic cell?

(*b*) How would you show that ions move in a solution which contains electrodes?

11. (*a*) What suggests strongly that electrolytes are dissociated into radicals, even when no electric potential is applied to the solution? Explain.

(*b*) How would the existence of independent radicals in solution explain the more rapid reactions of electrolytes?

12. (*a*) What conclusion may be drawn in regard to electrolytes by considering the magnitude of the effects they produce in the freezing point and boiling point of their solutions?

(*b*) Could the early explanations of the manner of ion formation account for the abnormal effects in the physical properties of solutions of electrolytes? Explain.

13. (*a*) State the two ideas of the Arrhenius theory.

(*b*) How did the Arrhenius theory account for the conductivity of solutions of electrolytes?

(*c*) Explain electrolysis and electrodeposition by the ionization theory with an example.

(*d*) Account for Faraday's Laws by means of the charges on the ions.

(*e*) How does the ionization theory account for the fact that all nickel salts give green solutions?

(*f*) Why are ionic reactions almost instantaneous?

(*g*) Explain voltaic action by the Arrhenius theory.

(*h*) How did Arrhenius account for the abnormal effect of electrolytes on the physical properties of solutions?

Chapter **23**

Acids, Bases, and Salts

1. Introduction. The early chemists arranged certain substances into two groups: one possessed properties like those of vinegar, while the other had the properties of ashes. The substances in the first group were known as *acids*, while those in the second were called *alkalis*. It was seen that the properties of acids and alkalis were opposed to one another, and that when they were combined one neutralized the other. The reaction between an acid and an alkali produced a substance known as a *salt*. It was further found that some substances possessed alkaline qualities, but unlike the alkalis, did not melt on heating and were almost insoluble in water. These substances received the name of *earths*. In 1774 Rouelle introduced the term *base* to denote all substances, including alkalis and earths, which reacted with acids to produce a salt.

2. The properties of acids. Lavoisier observed that certain elements produced oxides which when combined with water formed acids. These are known as acidic oxides and they react with basic oxides to form salts. Carbon forms carbon dioxide which with water produces carbonic acid. Similarly, sulphur dioxide produces sulphurous acid, and phosphorus pentoxide forms phosphoric acid. Other acidic oxides are B_2O_3, SiO_2, N_2O_3, P_2O_3 and SO_3. All acids contain hydrogen, which is the characteristic element in their reactions and is replaced by a metal during the formation of a salt. While all acids contain hydrogen, not all of them contain oxygen. The acids which contain oxygen are known as the *oxy-acids*,

while those which do not contain that element are known as the *hydracids*. The following list contains the names and formulas of the common acids.

TABLE 19—NAMES AND FORMULAS OF SOME COMMON ACIDS

Hydracids		*Oxy-acids*	
Hydrochloric acid	HCl	Sulphuric acid	H_2SO_4
Hydrobromic acid	HBr	Nitric acid	HNO_3
Hydriodic acid	HI	Carbonic acid	H_2CO_3
Hydrosulphuric acid	H_2S	Phosphoric acid	H_3PO_4
Hydrocyanic acid	HCN	Acetic acid	$HC_2H_3O_2$

From a study of the formulas of the acids given in the above list, it is seen that they all consist of hydrogen combined with a non-metal or a radical. The radical is usually composed of non-metallic elements, but it may occasionally contain a metal and it is referred to generally as the "acid radical".

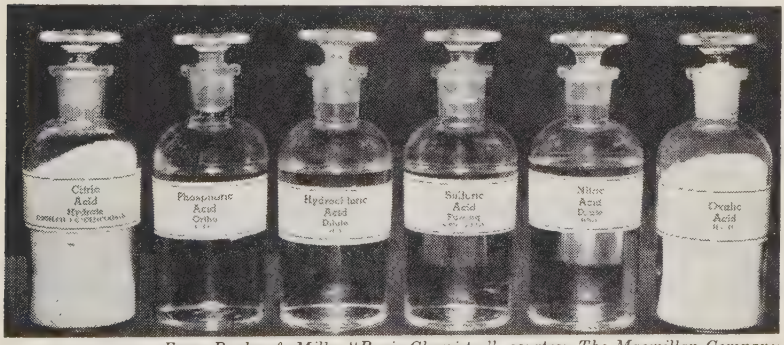


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Fig. 119. The common acids all yield hydrogen ions in solution.

The hydrogen in an acid can be replaced by a metal and it is this replacement reaction which produces a salt. Sometimes there are hydrogen atoms in an acid which are not capable of being replaced by a metal. This is the case with acetic acid, where only one of the four hydrogen atoms present in the molecule can be replaced by a metal. In writing the formula of an acid it is customary to place the replaceable hydrogen

first. Acetic acid, CH_3COOH, is an organic acid which contains the radicals "CH_3" and "COOH", and in organic chemistry it is customary to arrange the formulas so as to show the radicals which are present. In inorganic chemistry the formula of acetic acid is usually written as $HC_2H_3O_2$.

The number of replaceable hydrogen atoms determines the *basicity* of the acid. An acid with *one* replaceable hydrogen atom is said to be *monobasic*; an acid with *two* such atoms is known as *dibasic*; while an acid possessing *three* is called *tribasic*. Acids with more than three replaceable hydrogen atoms are not common.

The taste of vinegar, which is dilute acetic acid, is well known, and people use the expression "an acid taste" in their indentification of substances. The characteristic sour taste possessed by vinegar is a property of all the common acids. Very dilute solutions of the common laboratory acids may be tasted if desired, but indiscriminate tasting of substances in a laboratory may prove dangerous, or at the least, unpleasant.

When acids dissolve in water they dissociate into their two chief components, the hydrogen and the acid radical, each of which becomes an ion. The hydrogen ion has a positive charge of 1, while the other ion bears a negative charge as indicated by the valence of the acid radical. The production of hydrogen ions on solution in water is therefore a characteristic property of all acids. Each replaceable hydrogen atom in the formula of the acid will produce one hydrogen ion. The non-replaceable hydrogen atoms do not produce hydrogen ions but form part of the negative ion. The following equilibria illustrate the production of ions by acid:

$$HCl \rightleftarrows H^+ + Cl^-$$

$$H_2SO_4 \rightleftarrows 2\ H^+ + SO_4^{--}$$

$$H_3PO_4 \rightleftarrows 3\ H^+ + PO_4^{---}$$

$$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$$

The presence of hydrogen ions in an aqueous solution turns *blue* litmus paper *red*. Litmus paper is an unsized paper, like fine quality blotting paper, which is soaked with an infusion of a colouring matter prepared from certain lichens and known as *litmus*. Since acids produce hydrogen ions in aqueous solutions the solutions of all acids will turn blue litmus paper red. Litmus is one of a group of substances known as indicators, which are used to determine the presence of acids or bases by means of the colour change which is produced by a solution. Some of the common indicators used in the laboratory besides litmus are *methyl orange*, *methyl red* and *phenolphthalein*. The different indicators not only give various colour changes but change their colour at different concentrations of hydrogen ion (see Chap. 25, sec. 4). The ability of a solution of an acid to change the colour of an indicator is therefore a property of an acid.

Dilute acids have little effect on the skin except where it is broken, when they produce a smarting sensation. Concentrated acids produce considerable effects and their contact with the skin should be avoided. Concentrated sulphuric acid will remove water from animal tissue, leaving the carbon, which results in a blackening; nitric acid causes a yellow stain on skin and wool which cannot be removed by washing. All concentrated acids produce a burning effect on parts of the skin not usually protected by clothing, and acids have an injurious effect on most textiles. All acids should be regarded as poisons and great care should be taken lest they come in contact with the eyes and the mucous membranes of the nose and mouth.

The properties of acids may be summed up as follows:

(1) They all contain hydrogen which may be replaced by a metal to form a salt.
(2) They have a sour taste.
(3) They affect indicators. They turn blue litmus red.
(4) When dissolved in water they furnish hydrogen ions.

3. The preparation of acids. The general method of preparing an acid is to heat a salt of the acid with another acid which has a higher boiling point than the acid that is to be produced. Since sulphuric acid has a higher boiling point than most of the common acids, it is usually employed in the laboratory preparation of other acids. For example, hydrochloric acid and nitric acid may be made by heating a chloride and a nitrate, respectively, with sulphuric acid.

$$KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl$$
$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

In some cases, however, the general method cannot be used, as sulphuric acid may react with the acid which it is desired to produce.

4. The properties of bases. The term *base* is used generally to include all those substances which combine with acids to form salts, but it is usually confined to a group of compounds known as the *hydroxides*. The common bases and their formulas are given below:

Potassium hydroxide	KOH
Sodium hydroxide	NaOH
Ammonium hydroxide	NH_4OH
Calcium hydroxide	$Ca(OH)_2$
Barium hydroxide	$Ba(OH)_2$

It will be seen that these substances consist of a metal, or a metallic radical, combined with the *hydroxyl* radical, OH. The ammonium radical, NH_4, is classed as a metallic radical since it acts like a metal in all its reactions. The characteristic part of a hydroxide is the *hydroxyl radical*. This radical may be considered as being replaceable by an acid radical to form a salt. The number of hydroxyl radicals determines the *acidity* of the base, so that we have *monoacidic*, *diacidic* and *triacidic* bases.

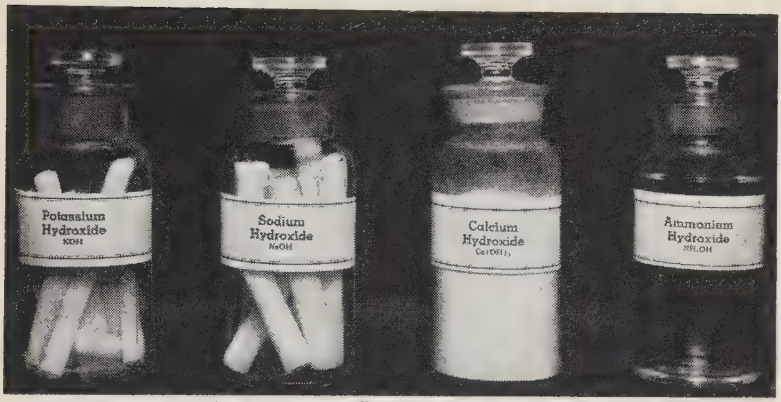

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Fig. 120. The common bases all yield hydroxyl ions when dissolved.

Solutions of bases produce an unpleasant softening effect on the mucous membranes of the mouth, but cannot be considered as having a particular taste. They all produce a characteristic "soapy" feel when rubbed between the fingers.

When hydroxides dissolve in water they dissociate into their components, the metal and the hydroxide radical, each of which becomes an ion. The metal ion or the ammonium ion always carries a positive charge indicated by its valence, and the *hydroxyl ion* bears a negative charge of 1. The production of hydroxyl ions in water is therefore a characteristic property of all hydroxides which are soluble, and each hydroxyl radical in the formula produces one hydroxyl ion. The following equilibria illustrate the production of ions by hydroxides.

$$KOH \rightleftarrows K^+ + OH^-$$
$$NH_4OH \rightleftarrows NH^+_4 + OH^-$$
$$Ca(OH)_2 \rightleftarrows Ca^{++} + 2\ OH^-$$

The presence of hydroxyl ions turns *red* litmus paper *blue*. As in the case of the solutions of acids, indicators undergo their particular colour change at different concentrations,

in this case, of hydroxyl ions. The ability to produce a colour change in indicators is therefore a property of hydroxides.

According to their concentration, hydroxides soften and disperse animal tissues to varying degrees. Concentrated solutions will destroy dead tissue and cause serious burns on living skin but dilute solutions produce only a "soapy" feeling when rubbed between the fingers. Alkalis also help to convert fats into soaps and glycerine thus loosening any dirt which is being held to the skin or a fabric by means of animal or vegetable oils. These properties make them important cleansing agents.

The properties of bases may be summed up as follows:

(1) They all contain the hydroxide radical which may be replaced by a non-metallic atom or radical to form a salt. In this respect the term "base" is limited to the hydroxides.
(2) They have a soapy feel.
(3) They affect indicators. They turn red litmus paper blue.
(4) When they dissolve in water the hydroxides furnish the hydroxyl ion.

5. Amphoteric hydroxides. Some metallic hydroxides can act either as a base or as an acid and are known as *amphoteric hydroxides*. When acting as bases their formulas are usually written so as to indicate that they contain the hydroxyl group and will produce that ion when they ionize. In the case of the hydroxides of zinc and aluminum we have the following reactions which are typical of those of a base when reacting with an acid.

$$\mathbf{Zn(OH)_2 + 2\ HCl \longrightarrow ZnCl_2 + 2\ H_2O}$$
$$\mathbf{Al(OH)_3 + 3\ HCl \longrightarrow AlCl_3 + 3\ H_2O}$$

When these substances act like an acid we write their formulas so as to indicate that they supply hydrogen ion when they ionize. In the case of the hydroxides of zinc and aluminum we may write them as H_2ZnO_2 and H_3AlO_3 and they can be shown as reacting with bases by the following equations.

$$H_2ZnO_2 + 2\ NaOH \longrightarrow Na_2ZnO_2 + 2\ H_2O$$
$$H_3AlO_3 + NaOH \longrightarrow NaAlO_2 + 2\ H_2O$$

The oxides from which such hydroxides are formed are called amphoteric oxides and the metals are said to show amphoteric behaviour. Among the common metals to do so are aluminum, tin, zinc, arsenic, antimony, bismuth, manganese, chromium, and to a slight extent iron and lead. These metals will appear both as cations and as anions in their compounds. Note zinc and aluminum above and the following pairs of formulas: SnO, Na_2SnO_2; As_2O_3, Na_3AsO_3; Sb_2O_3, Na_3SbO_3; Bi_2O_3, Na_3BiO_4; MnO, $KMnO_4$; Cr_2O_3, Na_3CrO_3. More information about the amphoteric properties may be found in the chapters devoted to the various metals and non-metals.

6. The preparation of bases. In general, hydroxides are produced by the action of metals or metallic oxides on water.

$$2\ Na + 2\ H_2O \longrightarrow 2\ NaOH + H_2$$
$$K_2O_2 + 2\ H_2O \longrightarrow 2\ KOH + O_2$$

The metallic oxides which unite with acidic oxides to form salts are called basic oxides, e.g., CaO, Na_2O, K_2O, MgO, Ag_2O, CuO, NiO, SrO and BaO. These basic oxides unite with water to form hydroxides. The soluble hydroxides are known as alkalis, the most common being sodium and potassium hydroxides. Barium hydroxide is used commonly in chemical analysis and calcium hydroxide solution is often known by the name "limewater". Most of the metallic hydroxides are insoluble or only slightly soluble in water, and may be prepared by precipitation on the addition of a soluble hydroxide to a solution of a salt.

$$FeCl_3 + 3\ NaOH \longrightarrow Fe(OH)_3 + 3\ NaCl$$
$$CuSO_4 + 2\ NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

7. The properties of salts. The substances produced by the reaction between an acid and a base are known as *salts*. They may be considered as being an acid in which the replaceable hydrogen atoms have been replaced by a metal, or as a base in which the hydroxyl radicals have been replaced by a non-metal or an acid radical. In considering them as being derived from an acid, we may, for example, speak of the sulphates as being the salts of sulphuric acid, and there will be a series of sulphates, each formed from that acid by the replacement of hydrogen by a different metal. On the other hand, if we think of them as being derived from a base we shall have a series of salts associated with a certain metal and formed by the replacement of the hydroxyl radical by different acid radicals or non-metals. We may speak of the salts of sodium, the salts of copper, and so on. The salts are considered usually from both points of view but the student may get a better idea of their formation if he associates them with an acid in which the hydrogen has been replaced. Salts therefore consist of two chief components, the metal and the non-metal or acid radical.

The salts have no properties which are common to all, but have properties belonging to the metal and the acid radical or non-metal of which they are composed. We find that the various salts of a particular metal have many properties in common; likewise do the salts of a particular acid. These properties are considered in the study of the acids and metals and will not be discussed here.

8. Acid salts and basic salts. If we consider the formation of a salt as the replacement of hydrogen atoms of an acid by a metal, we are faced with the possibility that when there is more than one hydrogen atom present in the acid all of these hydrogen atoms may not be replaced. If we have a salt which still contains replaceable hydrogen atoms it is known as an *acid salt*.

If sodium chloride is heated gently with sulphuric acid, one of the two replaceable hydrogen atoms in the sulphuric acid will be replaced by sodium, giving an acid salt.

$$\mathbf{NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl}$$

This salt is known as *sodium bisulphate*, *sodium acid sulphate*, or *sodium hydrogen sulphate*. If this acid salt be heated with sodium chloride, a further replacement occurs and the *normal salt*, sodium sulphate, is produced.

$$\mathbf{NaCl + NaHSO_4 \longrightarrow Na_2SO_4 + HCl}$$

In a similar manner we have two salts of carbonic acid, *sodium bicarbonate*, $NaHCO_3$, and *sodium carbonate*, Na_2CO_3. The idea of partial replacement can be seen if we look at the formulas of the salts:

Acid salts	*Normal salts*
$NaHCO_3$	Na_2CO_3
$NaHSO_4$	Na_2SO_4

In the case of phosphoric acid, H_3PO_4, since there are three replaceable hydrogen atoms in the formula we see that there are the possibilities of replacing one, two or three hydrogen atoms. All three salts of phosphoric acid are known (see Chap. 36, sec. 10).

In a similar manner *basic salts* are formed when not all of the hydroxide radicals are replaced by acid radicals or non-metals. In the case of lead hydroxide the hydroxide radicals can be replaced one at a time as shown below.

Lead hydroxide	$Pb(OH)_2$
Basic lead nitrate	$Pb(OH)NO_3$
Normal lead nitrate	$Pb(NO_3)_2$

While most dibasic and tribasic acids furnish acid salts as well as the normal salt, diacidic and triacidic bases do not always produce basic salts. Basic salts containing two OH radicals sometimes lose a molecule of water to form the *oxy-salts*.

Basic bismuth chloride yields bismuth oxychloride and water.

$$Bi(OH)_2Cl \longrightarrow BiOCl + H_2O$$

Basic antimony chloride yields antimony oxychloride and water.

$$Sb(OH)_2Cl \longrightarrow SbOCl + H_2O$$

9. The preparation of soluble salts. There are four general methods for preparing soluble salts: the action of an acid on metals, on metallic oxides, on hydroxides, and on carbonates. In the following examples the same salt, zinc chloride, will be prepared in each case.

(1) *The action of an acid on a metal.* If the metal is above hydrogen in the electro-chemical series (see Chap. 38, sec. 6), hydrogen will be displaced from the acid and the salt formed. If the metal is below hydrogen the salt will only be formed with oxidizing acids like nitric or sulphuric and the acid will be reduced. (See the equations below.) There are some noble metals, however, which do not react directly with any single acid.

$$Zn + 2\ HCl \longrightarrow ZnCl_2 + H_2$$
$$3\ Cu + 8\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 2\ NO + 4\ H_2O$$

(2) *The action of an acid on a metallic oxide.* Most metallic oxides react with acids to produce a salt and water.

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$
$$ZnO + 2\ HCl \longrightarrow ZnCl_2 + H_2O$$

Some natural occurring oxides as cuprous oxide, Cu_2O, and alumina, Al_2O_3, are very hard to dissolve in acids.

(3) *The action of an acid on a hydroxide.* Acids react with hydroxides to produce a salt and water. This is a general reaction known as *neutralization.* A study of this reaction shows that it consists of the hydroxyl radical of the base

combining with the hydrogen of the acid, to form water. No matter what base and what acid is used, neutralization results in the formation of water. This is shown by the measurement of the heat of reaction which shows that the same number of calories are liberated for every molecule of water formed, no matter what substances are involved in the reaction.

$$Ba(OH)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2\ H_2O$$
$$Zn(OH)_2 + 2\ HCl \longrightarrow ZnCl_2 + 2\ H_2O$$

(4) *The action of an acid on a carbonate.* The action of an acid on a carbonate is the reaction for the preparation of carbonic acid from one of its salts. The heat of the reaction is always sufficient to decompose the carbonic acid, so that carbon dioxide and water are always produced.

$$Na_2CO_3 + 2\ HNO_3 \longrightarrow 2\ NaNO_3 + H_2O + CO_2$$
$$ZnCO_3 + 2\ HCl \longrightarrow ZnCl_2 + H_2O + CO_2$$

10. The preparation of insoluble salts. The foregoing methods cannot be used when the desired salt is insoluble in water. If it is desired to produce a salt a solubility table must be consulted to discover whether or not the salt is soluble in water. If it is soluble, any of the four preceding methods may be employed; if it is not soluble, it must be prepared by *precipitation.* In this method of preparation the required salt is produced by the union of its component parts in solution. Since the salt is insoluble, it will be thrown down to the bottom of the vessel as soon as it is formed. An insoluble solid which is produced and thrown down to the bottom of the vessel in this manner is known as a *precipitate.*

To apply this method it must be remembered that a salt is composed of a metal and a non-metallic portion, and that both of these components must be present in the solution in the form of ions before precipitation can take place. The

consideration of these facts provides the general rule for the preparation of an insoluble salt: *add a solution containing the metallic ion to a solution containing the required non-metallic ion.* On mixing the two solutions, precipitation will occur. Since the hydroxyl radical is obtainable in solution as an ion, insoluble hydroxides may be prepared by this method.

If it is desired to prepare the insoluble salt *barium sulphate* the following procedure is employed. With the aid of the solubility table a *soluble barium salt* is selected. This salt will supply the metallic portion of the barium sulphate and *any soluble salt of barium* will suffice. Barium chloride is a convenient choice as it is a well-known barium salt and is soluble. Now a soluble sulphate is selected. Any will do, and since the salts of ammonium, sodium and potassium are mostly all soluble in water, sodium sulphate will be suitable. When solutions of the two chosen salts are added together barium sulphate will be precipitated.

$$BaCl_2 + NaSO_4 \longrightarrow \underline{BaSO_4} + 2\ NaCl$$

As another example, if it is desired to produce the insoluble salt silver chloride, any soluble silver salt and any soluble chloride may be chosen to supply the necessary ions. Although the insoluble substance which is produced is not ionized it must be obtained by selecting the ions which will be required for its production. Silver chloride will therefore be precipitated by the union of any soluble silver salt and any soluble chloride. We can, for example, choose silver nitrate and potassium chloride.

$$AgNO_3 + KCl \longrightarrow \underline{AgCl} + HNO_3$$

In these equations which represent precipitation the insoluble substance is indicated usually by an underline. In some texts a downward arrow is placed after the formula of the precipitate.

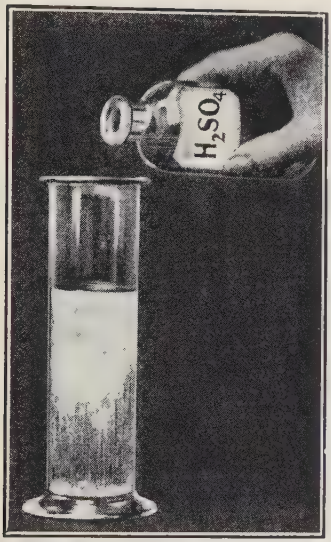

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Fig. 121. Sulphuric acid and barium chloride produce insoluble barium sulphate.

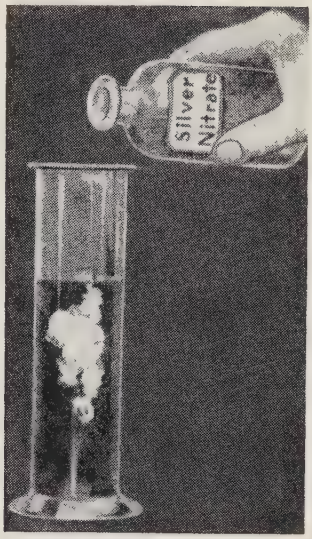

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Fig. 122. Silver nitrate and potassium chloride produce insoluble silver chloride.

If it does not cause decomposition of any of the substances in the reaction an acid may be used instead of a salt to provide the negative ions. In the example given above, sulphuric acid could be used in the precipitation of barium sulphate, and hydrochloric acid in the precipitation of silver chloride.

Insoluble salts may be produced in the dry way by the interaction of an acidic and a basic oxide.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

Often one acidic oxide is used to displace another as in the making of sodium silicate or phosphorus.

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$

$$Ca_3(PO_4)_2 + 3\ SiO_2 \longrightarrow 3\ CaSiO_3 + P_2O_5$$

Question Summary

1. What early distinction was made between acids and alkalis?

2. (*a*) What was the acid theory of Lavoisier and why was it abandoned? What are acidic oxides?
(*b*) Give examples of hydracids and oxy-acids. Indicate the basicity of each acid.
(*c*) What are indicators? Name some of them.
(*d*) List the properties of acids.

3. What is the general method for preparing an acid? Write equations to give some examples.

4. (*a*) Write the formulas of some well-known bases. Indicate the acidity of each base.
(*b*) List the properties of bases.

5. (*a*) What is an amphoteric hydroxide?
(*b*) Write equations showing the reactions of amphoteric hydroxides.

6. (*a*) What is the usual method of preparing hydroxides?
(*b*) What are basic oxides?

7. Discuss the properties of salts.

8. (*a*) Define an acid salt, a basic salt, an oxy-salt.
(*b*) Give the formulas for the sodium salts of phosphoric acid.

9. Give the methods of preparing soluble salts.

10. Give methods of preparing insoluble salts.

Chapter **24**

Working with Electrolytes

1. Introduction. You have been introduced in a general way to our modern ideas about solutions of electrolytes but we have not given you many examples of how their concentration is expressed or how their properties vary with the concentration. We will now try to show you how these defined concentrations are realized in practice and how they are used to compare conductivities. We will also try to tell you something about writing ionic equations and predicting the results of ionic reactions.

2. Making empirical solutions. When empirical methods are used to express the concentration of a solution it is often difficult for a chemist to make calculations about the quantity required for a reaction. For example, a 10% NaCl solution may be specified for use. This means that it contains 10 g. of NaCl in 100 g. of solution but solutions are usually measured by volume so it is necessary to know the *density* of the solution in order to calculate the volume which weighs 100 g. Engineers have to become proficient at such calculations which are largely a matter of careful thinking and simple arithmetic. Chemists like to work with molar and normal solutions but they often have to prepare solutions of empirical concentrations. We say the *concentration* of such solutions is *expressed in physical units* and some of the arithmetical manipulations used in preparing and using them are illustrated below.

Example 1. How would you prepare 120 ml. of a solution of $AgNO_3$ to contain 5 mg. per ml.?

The quantity for 120 ml. is $5 \times 120 = 600$ mg.

We would weigh out 600 mg. or 0.600 g. and dissolve it in enough water to make 120 ml. of solution when thoroughly mixed.

Example 2. Concentrated nitric acid has a specific gravity of 1.42 and contains 70% HNO_3 by weight. How many grams of nitric acid are contained in 1 litre?

(*i*) One litre weighs $1.42 \times 1000 = 1420$ g.

(*ii*) One litre contains $1420 \times .70 = 994$ g. of HNO_3.

Example 3. How many millilitres of a 37% HCl solution would you add to a beaker when the directions call for adding 3 g. of HCl? The density of this HCl solution is 1.2 g./ml.

(*i*) The weight of 1 ml. of HCl is 1.2 g. so 1 ml. contains $1.2 \times \frac{37}{100} = .444$ g. of HCl.

(*ii*) To add 3 g. we need $\frac{3.000}{0.444} = 6.78$ ml. of HCl solution.

3. Making molar solutions. *A molar solution* contains one *formula weight of solute per litre of solution.* You have seen in Chap. 11 how the formula weight is calculated by adding up the atomic weights. We may express the concentration of any solution as a fraction of a molar solution.

Example 4. A one molar (M) solution of H_2SO_4 contains 98.08 g. of H_2SO_4 per litre of solution. Calculate the weight of sulphuric acid required to make a litre of 0.2 M solution.

Solution of problem. The solution must contain $0.2 \times 98.08 = 19.616$ g. of H_2SO_4 and this will be added to enough water to make the *total volume* up to one litre.

Example 5. Calculate the weight of $NaNO_3$ required to make 200 ml. of 0.4 M solution.

Solution of problem.

Step I. The solution must contain $0.4 \times [(23 + 14 + (3 \times 16)]$ g. of $NaNO_3$ per litre of solution. This is $0.4 \times 85 = 34$ g.

Step II. For 200 ml. of this solution we would require $\frac{200}{1000} \times 34 = 6.8$ g. of $NaNO_3$ in enough water to make 200 ml. *of solution.*

A molar solution describes the concentration of a solution in chemical unit quantities without reference to the reaction the solute might undergo.

4. Making normal solutions. A normal solution contains *one gram equivalent weight per litre of solution.* We must first learn to calculate *the equivalent weight of a compound* because most substances are weighed out as compounds in the pre-

paration of solutions. The equivalent weight of an element was found in Chap. 11, sec. 3 to be given by

$$\frac{\text{Atomic Weight}}{\text{Valence}}$$

The equivalent weight of a compound may be found in the same way.

$$\frac{\text{Formula Weight}}{\text{Valence}}$$

Now in a compound we have many atoms with different valences so we must choose one of them before we can find the equivalent weight. This is done by considering the reaction for which the solution is prepared. Acids are prepared for neutralization reactions so we look for the total valence of the hydrogen atoms because they provide the acid ions. Hydrogen chloride provides one equivalent weight of hydrogen ion per molecular weight so we say the valence for the compound is one.

Example 6. What is the gram equivalent weight of HCl?

$$\text{Gram equivalent weight} = \frac{1.008 + 35.457}{1} = 36.465 \text{ g.}$$

Example 7. Calculate the gram equivalent weight of H_2SO_4.

One formula weight of H_2SO_4 contains *two* equivalent weights of hydrogen so the valence is two.

$$\text{Gram equivalent weight} = \frac{2.016 + 32.06 + 64.00}{2} = 49.038 \text{ g.}$$

Example 8. Calculate the equivalent weight of $AlCl_3$.

Aluminum chloride might be used in a precipitation reaction with sodium hydroxide to form $Al(OH)_3$ or the chloride might be all precipitated with silver nitrate. In the first reaction the three positive charges on the aluminum ion enable it to accept three OH^- ions to form $Al(OH)_3$. In the second reaction each chloride ion from $AlCl_3$ accepts one silver ion from $AgNO_3$. In either case one formula weight of $AlCl_3$ requires three equivalents. The gram equivalent weight is

$$\frac{26.97 + (3 \times 35.457)}{3} = 44.41 \text{ g.}$$

Thus 44.41 g. of aluminum chloride dissolved in enough water to make a litre of solution is a one normal solution for such reactions.

For bases we note the number of OH ions they can produce by dissociation. In general we may *note the total valence of the positive or negative ions the compound can produce when it dissociates in water.*

Example 9. Calculate the gram equivalent weight of (*a*) NaCl (*b*) $CaCl_2$ (*c*) $Na_3PO_4.12H_2O$ (*d*) $Ca_3(PO_4)_2$.

We may say that in general the gram equivalent weight of a compound is the weight which contains one gram equivalent weight of either the metal or negative radical.

In (*a*) valence of Na = 1.

Weight of NaCl to give one gram equivalent of Na = 58.45 g. This is the gram equivalent weight of NaCl.

In (*b*) valence of Ca = 2 so the equivalent weight of calcium is one-half the atomic weight. The weight of $CaCl_2$ which will contain one-half of an atomic weight of calcium is one-half mol.

Gram equivalent weight of $CaCl_2 = \frac{1}{2} \times 110.99$ g. = 55.50 g.

In (*c*) valence of $PO_4 = 3$. The gram equivalent weight is one-third of the formula weight or $\frac{1}{3} \times 380.16 = 126.72$ g. Note that the formula weight contains the weight of the water of hydration because this is weighed with the salt in making up solutions.

In (*d*) valence $= 3 \times 2 = 6$.

The gram equivalent weight is one-sixth of the formula weight or $\frac{1}{6} \times 310.2$ g. = 51.70 g. Note that each calcium ion has a valence of two and there are three of them in the formula.

Once the equivalent weight has been determined the making of normal solutions is the same as that for the empirical and molar solutions.

Example 10. How would you prepare a litre of 1 normal (N) NaOH?

Since the valence of sodium is 1 each formula weight contains one equivalent weight. The equivalent weight is 22.997 + 16 + 1.008 = 40.005 g. This weight is dissolved in enough water to make one litre of solution.

Example 11. How many grams of HCl are needed to make 35 ml. of a 0.22 normal solution.

(*i*) The equivalent weight of HCl is 36.465 g.

(*ii*) A litre of 0.22 N solution would require 0.22×36.465 g. = 8.022 g.

(*iii*) For 35 ml. we would need $\frac{35}{1000} \times 8.022 = .281$ g. This weight would be dissolved in enough water to make 35 ml. of homogeneous solution.

Example 12. What weight of copper sulphate, $CuSO_4.5\ H_2O$, is needed to prepare 300 ml. of a 0.5 N solution for a reaction where the copper suffers a valence change of two units?

(*i*) Since the valence change is 2, the equivalent weight is one-half the formula weight.

$$\frac{63.57 + 32.06 + (4 \times 16.00) + (5 \times 18.016)}{2} = 124.85 \text{ g.}$$

(*ii*) For a 0.5 N solution we require $124.85 \times 0.5 = 62.43$ g. per litre.

(*iii*) For 300 ml. of a 0.5 N solution we would need $\frac{300}{1000} \times 62.43$ g. $= 18.729$ or 18.73 g. of $CuSO_4.5\,H_2O$.

Example 13. What is the normality of concentrated HCl if it has a density of 1.2 g. per litre and contains 37% of HCl by weight?

(*i*) One litre weighs $1.2 \times 1000 = 1200$ g.

(*ii*) One litre contains $1200 \times \frac{37}{100} = 444$ g. of HCl.

(*iii*) One litre contains $\frac{444}{36.465} = 12.18$ equivalent weights of HCl.

The solution is 12.18 N.

Example 14. What is the normality of a solution which contains 2.65 g. of Na_2CO_3 in 200 ml. of solution?

(*i*) We assume the Na_2CO_3 is to be completely neutralized so each mol will yield two equivalent weights. The gram equivalent weight is

$$\frac{(2 \times 23) + 12.0 + (3 \times 16.0)}{2} = 53 \text{ g.}$$

(*ii*) 2.65 g. in 200 ml. is the same concentration as $2.65 \times \frac{1000}{200} = 13.25$ g. per litre.

(*iii*) 13.25 g. per litre is $\frac{13.25}{53} \times 1 = 0.25$ N.

5. Dilution of solutions. Wherever the concentration of a solution is given in terms of weight per unit of volume, as in g./ml. or mols/l., it follows that the quantity of solute is given by multiplying the concentration by the volume. When a solution is diluted the quantity of solute is unchanged so we can say:

$$\mathbf{V_1 \times C_1 = V_2 \times C_2}$$

V_1 = volume before dilution — V_2 = volume after dilution

C_1 = concentration before dilution — C_2 = concentration after dilution

Example 15. How much water must be added to 200 ml. of a solution which contains 15 g. of solute per 100 ml. to make a solution containing 5 g. of solute per 100 ml.? Let X = volume after dilution.

(*i*) $200 \times 15 = X \times 5$ since $\text{volume}_1 \times \text{concentration}_1 = \text{volume}_2 \times \text{concentration}_2$.

(*ii*) Solving: $X = 600$ ml.

(*iii*) Water to be added; $600 - 200 = 400$ ml.

Example 16. 100 ml. of a solution of 20% H_2SO_4 which a table shows has a specific gravity of 1.14 is to be made by diluting 98% sulphuric acid which has a specific gravity of 1.84. How much of the concentrated acid is required? Note that we must express the concentration of both solutions

in grams per millilitre or similar units. Let X be the required volume of concentrated acid.

(*i*) In 20% solution there is $1.14 \times .20 = 0.228$ g./ml.

(*ii*) In 98% solution there is $1.84 \times .98 = 1.80$ g./ml.

(*iii*) $V_1 \times C_1 = V_2 \times C_2$ so $100 \times 0.228 = X \times 1.80$

$X = 12.7$ ml.

This must be carefully added to some water and the solution further diluted to 100 ml.

Example 17. How much 0.1 N HNO_3 could be prepared from 10 ml. of 15 N acid?

Normality is a method of expressing concentration in terms of weight per unit volume so it can be used in the equation $V_1 \times C_1 = V_2 \times C_2$. Let X be the volume of 0.1 N acid.

(*i*) $X \times 0.1 = 10 \times 15$

(*ii*) $X = 1500$ ml.

6. Molarity and normality. If we know the molarity of a solution we can tell its normality by noting the number of equivalent weights in each formula weight.

Example 18. Find the normality of 0.24 M H_2SO_4. Since 1 mol of H_2SO_4 contains 2 equivalent weights of replaceable hydrogen, the normality will be double the molarity. The normality is thus 0.48.

If a mol contains only one equivalent weight the normality is the same as the molarity.

7. Conductivity and the degree of ionization. You will recall that some solutions would conduct electricity better than others. In order to explain this, Arrhenius assumed that certain substances dissociated to a greater degree than others. The following table shows the apparent percentage dissociation of some common electrolytes. You will notice that they are compared in solutions which contain potentially the same number of ions per litre.

Since many of the reactions of electrolytes depend on the reactions between ions we refer to an acid or base which shows an apparently high percentage of its molecules to be ionized as a *strong* acid or base. We use the term *weak* to refer to an acid or base which appears to be slightly ionized. Because of this use for the terms *weak* and *strong*, they should not be used to indicate concentration, where the terms

TABLE 20—THE APPARENT DEGREE OF DISSOCIATION OF SOME ELECTROLYTES

(in tenth-normal aqueous solution, measured at 18°C.)

Acids	%	*Bases*	%
Hydrochloric acid	92.00%	Sodium hydroxide	91.00
Nitric acid	92.00	Potassium hydroxide	91.00
Sulphuric acid	61.00	Barium hydroxide	77.00
Phosphoric acid	27.00	Ammonium hydroxide	1.30
Acetic acid	1.30		
Carbonic acid	0.17	*Salts*	
Boric acid	0.01	Potassium chloride	86.00
		Sodium chloride	84.00
		Silver nitrate	81.00
		Sodium bicarbonate	78.00
		Barium chloride	76.00
		Cupric sulphate	41.00

dilute and *concentrated* should be used. Salts are almost all highly ionized, although a few, such as lead acetate and mercuric chloride show a small number of ions when in solution. The terms *weak* and *strong* are not usually applied to salts.

Arrhenius concluded that there was a greater degree of dissociation in dilute than in concentrated solutions and stated that maximum percentage dissociation occurred at infinite dilution. The increase in ionization with dilution is often demonstrated by taking a saturated solution of cupric bromide, which dissolves as brown molecules in concentrated solution, and pouring a little of it into a test tube full of water to dilute it. The dilute solution is blue like any other copper solution which contains cupric ions.

$$CuBr_2 \text{ molecules} \rightleftarrows Cu^{++} \text{ ions and } 2\ Br^{-} \text{ ions.}$$

This was explained by assuming that in dilute solution the distance between the ions would be greater than in a concentrated solution so that there would be less chance of the ions meeting one another and recombining to form mole-

cules. One of the limitations of the theory of Arrhenius was that many of the conclusions derived from it would not apply to concentrated solutions. An important modification of the original theory has been in connection with the apparent degree of dissociation. It is known as the Debye-Hückel theory.

8. The writing of equations in the ionic form. It is convenient to express many chemical equations in the form of ions. To do that it is necessary to follow closely several steps in the case of each formula of the equation in its turn. Let us write the following equation in ionic form:

$$2\ KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2\ H_2O$$

We shall start with the formula 2 KOH, as it appears in the equation, and consider the steps involved.

(1) *The type of ion produced.* Substances dissociate into positive and negative ions whose names correspond closely to the names of the original substances. *Potassium hydroxide* will dissociate into *potassium* and *hydroxide* ions.

$$K + OH$$

The *hydroxide* ion is usually called the *hydroxyl* ion. Notice that a "plus" sign is placed between the ions.

(2) *The placing of the electric charges. Hydrogen and all metals, or metallic radicals like the ammonium radical, are always positively charged. All others, no matter what they are, are negatively charged.* We therefore have the charges placed as:

$$K^+ + OH^-$$

(3) *The number of charges on each ion.* The number of charges on each ion is the same as that of the valence of the atom or radical from which the ion is formed. In the example, since the valence of potassium and the hydroxide is each one, we have one charge on each ion.

(4) *The numbers of each ion.* Since *each* atom or radical produces *one* ion, and since in our equation we have *two* potassium atoms and *two* hydroxide radicals, we shall have *two* ions of each.

$$2\ K^+ + 2\ OH^-$$

(5) *The number of positive charges must balance the number of negative charges.* If the positive and negative charges do not equal one another we know that we have made a mistake. If you find this to be the case, *do not try to alter the numbers but retrace your steps and find the mistake.*

Repeating these steps for each formula, and remembering that only *soluble* acids, bases and salts produce ions, we get the completed equation. Water, not being an acid, base or salt, will not ionize appreciably. We thus get the completed equation:

$$2\ K^+ + 2\ OH^- + 2\ H^+ + SO_4^{--} \longrightarrow 2\ K^+ + SO_4^{--} + 2\ H_2O$$

9. The reactions of acids, bases and salts in water. On examining the reactions of acids, bases and salts in aqueous solution it will be seen that the reaction equilibrium is disturbed so as to run to completion in three cases:

(1) the formation of a slightly ionized substance;

(2) the formation of an insoluble substance;

(3) the evolution of a gas.

Since we are considering reactions that occur in solution we are dealing with substances that may dissociate into ions. An examination of the three cases mentioned above show that, while they appear to be different from one another, they all represent the displacement of an equilibrium by the removal of a resultant. This must be borne in mind during a more detailed discussion of each case.

(1) *The formation of a slightly ionized substance.* The formation of water takes place during neutralization, where an acid reacts with a base to produce a salt. Let us write the

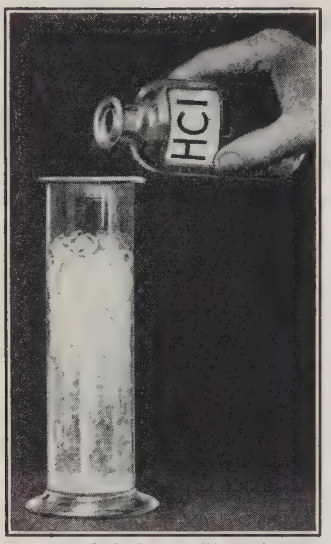

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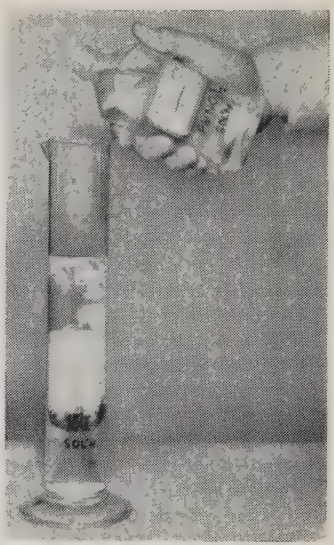
Fig. 123. Hydrochloric acid and sodium carbonate react completely because a gas is evolved.



From Bayles & Mills "Basic Chemistry", courtesy The Macmillan Company

Fig. 124. The reaction between lead nitrate and potassium iodide goes to completion because insoluble lead iodide is formed.

equation for a neutralization reaction in the form of ions, remembering that water is not ionized:

$$KOH + HCl \longrightarrow KCl + H_2O$$

$$K^+ + OH^- + H^+ + Cl^- \longrightarrow K^+ + Cl^- + H_2O$$

The ions in the solution are free to move in any direction, being attracted to and repulsed by one another according to the sign of the electric charges which they bear. The hydrogen ion is attracted by both the chloride and the hydroxyl ions; there is just as much chance of it joining with one as with the other. When ions unite with one another in solution they usually become dissociated later on and may subsequently form other unions. The result of these unions and dissociations is that there is always a supply of each ion in the solution. However, when the hydrogen ion unites

with the hydroxyl ion, they form the slightly ionized substance water and they cannot break apart, since water does not dissociate appreciably. They are, so to speak, removed from the ionic circulation. The formation of the slightly ionized water means that nearly all the hydrogen and hydroxyl ions are no longer available for union with the chloride and potassium ions, which have no choice but to unite with one another to form potassium chloride if the solvent is evaporated. Thus neutralization consists of the formation of water and a salt, no matter what acid and what base may be used. All neutralization reactions will thus proceed to completion since slightly ionized water is formed.

(2) *The formation of an insoluble substance.* Let us consider the formation of insoluble barium sulphate by the union of solutions of barium chloride and sodium sulphate, and express the equation in the form of ions.

$$BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2\ NaCl$$
$$Ba^{++} + 2\ Cl^- + 2\ Na^+ + SO_4^{--} \longrightarrow BaSO_4 + 2\ Na^+ + 2\ Cl^-$$

On mixing the two solutions we have the collection of ions shown on the left of the arrow in the above equation. The barium ions have a chance to unite with either the chloride or the sulphate ions. If they unite with the chloride ions they may subsequently break apart, but at any rate they will remain as ions within the solution. But when they unite with the sulphate ions they form a compound that is very little soluble, and they are thus removed from any further reaction in the solution, even though they may be in the solid that is lying on the bottom of the vessel. The sodium and chloride ions remain in the solution, and, since there are now no other ions present, they function as a solution of sodium chloride. All reactions which result in the formation of an insoluble substance will therefore proceed to completion because of the removal of ions from the solution (see Figures 121, 122 and 124).

(3) *The evolution of a gas.* In the case of the displacement of carbon dioxide from a carbonate by hydrochloric acid we can illustrate the reaction as follows:

$$Na_2CO_3 + 2\ HCl \longrightarrow 2\ NaCl + H_2O + CO_2$$
$$2\ Na^+ + CO_3^{=} + 2\ H^+ + 2\ Cl^- \longrightarrow 2\ Na^+ + 2\ Cl^- + H_2CO_3$$

Now H_2CO_3 is only our way of writing the dissolved form of CO_2 in water. Since CO_2 is only slightly soluble in water little of it remains as H_2CO_3 but decomposes into CO_2 and H_2O. The carbon dioxide escapes into the atmosphere and it is thus removed from solution. The carbonate ions which might reverse the reaction are continually destroyed. The equilibrium is displaced to the right. Since H_2CO_3 is only slightly ionized the reaction would run in the forward direction as in case (1), even if the solution were dilute enough to keep all the carbon dioxide dissolved. Heating would decrease the solubility of carbon dioxide and help to complete the reaction (see Fig. 123).

The reaction between completely soluble substances may be illustrated by the mixing together of solutions of potassium nitrate and sodium chloride, both of which are soluble in water. This is represented by the equation which shows the formation of potassium chloride and sodium nitrate, expressed as an equilibrium.

$$KNO_3 + NaCl \rightleftarrows KCl + NaNO_3$$
$$K^+ + NO_3^- + Na^+ + Cl^- \rightleftarrows K^+ + Cl^- + Na^+ + NO_3^-$$

On examining the left-hand side of the equation we find the following ions: potassium, sodium, nitrate and chloride, and since they are free to move about and unite with one another, we could expect to find potassium nitrate and sodium chloride, or potassium chloride and sodium nitrate produced in the solution. If we now examine the right-hand side of the equation we find exactly the same state of affairs.

Since both sides of the equation are alike we must indicate the existence of an equilibrium by the use of double arrows and must conclude that the reaction cannot go to completion in either direction. In this case an non-ionized substance is *not* produced and we find there is no reaction at all. We would also find that there is no evidence of any heat changes in the solution, showing that no chemical compounds are formed. We can therefore conclude that, to have a reaction go to completion, we must have the removal from the zone of reaction of one or more of the ions. This conclusion is of importance in predicting the reactions that may occur between electrolytes.

Question Summary

1. Describe briefly our modern ideas about electrolytes.

2. (*a*) What weight of $ZnCl_2$ is required to make
(*i*) 100 ml. of solution containing 10 mg./ml.?
(*ii*) 1200 g. of 7% solution?
(*b*) Glacial acetic acid, $H.C_2H_3O_2$, containing 97.8% of acetic acid by weight has a density of 1.05 g./ml. What is the concentration of the solution in grams per litre?
(*c*) How many grams of ammonia gas can be dissolved in each 100 g. of water if it makes a solution with a density of 0.89 g./ml. containing 28% of NH_3 by weight?

3. (*a*) How many grams of solid are required for a litre of 1 M solution of the following:
(*i*) NaOH, (*ii*) $MgSO_4.7H_2O$, (*iii*) $Al_2(SO_4)_3.12H_2O$?
(*b*) Find the molarity of the following solutions:
(*i*) 200 ml. of solution contains 9.8 g. of H_2SO_4.
(*ii*) 600 ml. of solution contains 5.3 g. of Na_2CO_3.
(*iii*) 1500 ml. of solution contains 100 g. of H_3PO_4.
(*c*) Calculate the weight of NaOH required to make
(*i*) 300 ml. of 0.5 M solution.
(*ii*) 2 litres of 0.25 M solution.

4. (*a*) Calculate the gram equivalent weight of
(*i*) zinc metal,
(*ii*) HNO_3 as an acid.
(*iii*) NaOH.
(*iv*) $Ca(OH)_2$.
(*v*) $AlPO_4$.

(*b*) How many gram equivalent weights of solute are needed to make
(*i*) one litre of 2 N solution?
(*ii*) 0.5 litre of 0.1 N solution?
(*iii*) 300 ml. of 0.4 N solution?

(*c*) How many grams of HCl are needed to make each of the three solutions in 4 (*b*)?

(*d*) How would you prepare the following solutions:
(*i*) one litre of 2 N NaCl?
(*ii*) 500 ml. of 0.4 N $FeCl_3$?
(*iii*) 25 ml. of 1.2 N Na_2CO_3?

(*e*) Calculate the normality of the solutions containing
(*i*) 24.52 g. of H_2SO_4 in one litre.
(*ii*) 37.46 g. of $CuSO_4.5H_2O$ in 600 ml.
(*iii*) 2.81 g. of HCl in 70 ml.

(*f*) What is the normality of solutions containing
(*i*) 35 ml. of 37% HCl of specific gravity 1.2 in one litre?
(*ii*) concentrated nitric acid which has a specific gravity of 1.44 due to 68% of HNO_3 by weight?
(*iii*) concentrated ammonia which has a specific gravity of 0.89 due to 28% of NH_3 by weight?

5. (*a*) How much water must be added to the following solutions to make solutions containing 10 g. per litre.
(*i*) 500 ml. of a solution containing 20 g. of solute?
(*ii*) 400 ml. of a solution containing 40 mg. per ml.?

(*b*) What volume of 0.1 N HCl can be made from 200 ml. of 1.5 N HCl?

6. What is the normality of the following solutions:
(*i*) 2M NaOH?
(*ii*) 0.2 M H_2SO_4?
(*iii*) 0.3 M H_3PO_4?
(*iv*) 0.11 M $CaCl_2$?
(*v*) one containing 1 mol of HCl in 250 ml.?

7. (*a*) What is meant by (1) a strong acid; (2) a weak base?

(*b*) Explain the difference in conductivity between weak and strong acids by the degree of dissociation.

8. Enumerate the steps for writing equations in the ionic form and illustrate them with a new example.

9. (*a*) Explain how the neutralization of barium hydroxide by nitric acid will go to completion.

(*b*) Explain how the precipitation of zinc carbonate from the addition of solutions of zinc nitrate and sodium carbonate will go to completion.

(*c*) Explain how the production of hydrogen sulphide by the action of hydrochloric acid on sodium sulphide will go to completion.

(*d*) Explain why the reaction between cupric sulphate and sodium chloride will not go to completion.

Chapter **25**

Ionic Equilibria

1. Introduction. Since ionization is a reversible process we are always disturbing an ionic equilibrium when we add one electrolyte to another or dissolve an electrolyte in water. We will see now that water itself is a very weak electrolyte and reacts with other electrolytes. We have already studied ionic equilibria in the apparent degree of ionization and the ways of making reactions run to completion so we can continue them here.

2. Ionization of water. The neutralization of weak acids and bases and the behaviour of their salts in water is influenced by the ions produced by the dissociation of water. *Water is a very slightly ionized substance* in terms of its percentage dissociation but there are so many molecules in every aqueous solution that there are at least a few hydrogen and hydroxyl ions present in every water solution. The equilibrium between water and its ions can be represented by

$$H_2O \rightleftarrows H^+ + OH^-$$

The numbers which can be present at any one time are determined by the fact that *the product of the number of hydrogen ions times the number of hydroxyl ions is always constant.* This constant is known as the ion-product constant of water. The numbers of each kind are measured in gram equivalent weights per litre and the product of their concentrations is equal to 10^{-14} when expressed in this way. We can say

Hydrogen ion concentration $\times$ Hydroxyl ion concentration $= 10^{-14}$

Now 10^{-1} is 1/10 and 10^{-2} is 1/100 and so on, so you can see that neither the hydrogen nor the hydroxyl ion concentration can be very large unless the other is extremely small.

Pure water would give equal numbers of hydrogen and hydroxyl ions as each molecule dissociated and this would then be a neutral condition. There would be 10^{-7} gram equivalent weights of hydrogen ion and 10^{-7} gram equivalent weights of hydroxyl ion in each litre of water since $10^{-7} \times 10^{-7} = 10^{-14}$. *A neutral solution is one which contains equal numbers of hydrogen and hydroxyl ions.* The number of ions is actually 10^{-7} times 6.03×10^{23} or 6.03×10^{16} of each kind per litre of water.

An acidic solution contains more hydrogen ions than hydroxyl ions. Thus when a little HCl is added to water the hydrogen atom yields an electron to the chlorine atom and the water insulates the charged ions from one another (see Chap. 15 or Chap. 32).

$$\mathbf{HCl \longrightarrow H^+ + Cl^-}$$

This increases the hydrogen ion concentration in the water and the ionization of the water is reversed. The equilibrium

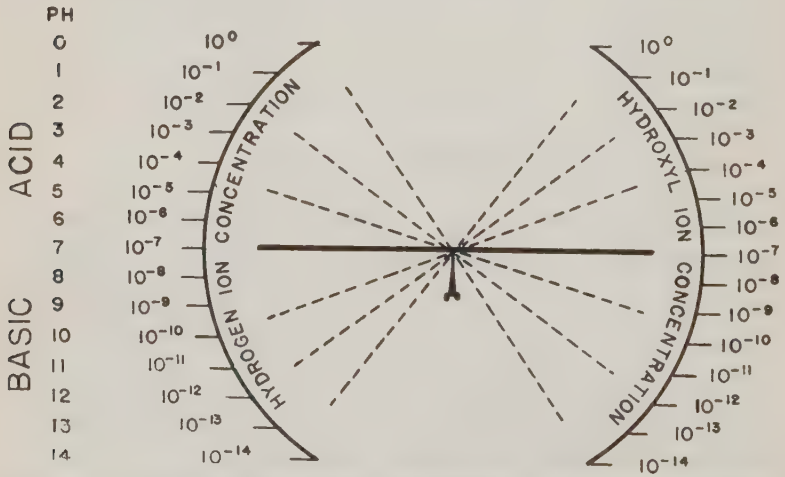


Fig. 125. When the hydrogen ion concentration increases the hydroxyl ion concentration decreases and vice versa.

is displaced until the hydroxyl ion concentration is small enough to make the product of the concentrations equal to 10^{-14}. If the hydrochloric acid raises the hydrogen ion concentration to 1/1000 gram equivalent weights per litre or 10^{-3}, then the ionization of water will be repressed until the hydroxyl ion concentration is only 10^{-11} gram equivalent weights per litre.

A basic solution contains more hydroxyl ions than hydrogen ions. When a little NaOH is dissolved in water it ionizes

$$\mathbf{NaOH \longrightarrow Na^+ + OH^-}$$

The increase in OH^- ions reverses the ionization of water until equilibrium is again restored.

$$\mathbf{H_2O \longleftarrow H^+ + OH^-}$$

The hydrogen ions are recombined to form water. If the NaOH raises the OH^- concentration to 10^{-2} gram equivalent weights per litre then the hydrogen ion concentration is reduced to 10^{-12} gram equivalent weights per litre. These changes are illustrated by the "sea-saw" diagram in Fig. 125.

3. Measurement of acidity and basicity. The concentrations of hydrogen and hydroxyl ion in water solutions are so small that their representation is an awkward problem. We have used negative powers of ten to indicate these small fractions but even these were found to be too cumbersome so only *the numerical part of the negative power of ten* is used. *It is called the pH.* If the hydrogen ion concentration of a solution is 10^{-3} gram equivalent weights per litre we say the pH is 3. This means that the smaller the pH the greater is the acidity and the larger the pH the less the acidity. A neutral solution has a pH of 7.

The hydroxyl ion concentration is determined by the hydrogen ion concentration because their product is constant,

so it is possible to *represent the strength of basic solutions by their hydrogen ion concentration.* It is always less than 10^{-7} gram equivalent weights per litre; hence the pH of basic solutions is always greater than 7. You will learn in your mathematics courses that any fraction can be expressed as a negative power of ten; therefore any hydrogen ion concentration can be indicated by a number. The pH is thus the simplest way to describe the acidity or basicity of a solution. This is indicated by the diagram in Fig. 125.

The pH is the most widely used method of indicating acidity. When we say that the pH of the gastric juice is 1.9 we indicate that it is an acidic solution containing more than 1/100 gram equivalent weights of hydrogen ion and less than 10^{-12} gram equivalent weights of OH^- ion per litre. When we say the pH of a sodium carbonate solution is 10.2 we indicate that it is a basic solution. Solutions with pH values between 7 and 14 are increasingly basic; between 7 and 0 they are increasingly acidic.

Ingenious electrical instruments have been devised to measure the pH of solutions but the commonest method is by the use of acid-base indicators.

4. Indicators. We have already mentioned several indicators in Chap. 23, such as litmus, methyl orange, methyl red and phenolphthalein. These are organic substances which change their colour with the amount of hydrogen ion present in the solution. Some of them occur naturally, like litmus; some are synthetic. Some indicators require very little hydrogen ion to give them their acidic colour and some require a considerable amount. This is shown in Fig. 126. Litmus is one of the few indicators that changes colour at the neutral point; therefore it is widely used for testing solutions. Most indicators indicate various degrees of acidity or basicity over a limited range so it is customary to select the indicator for the particular pH we wish to detect. We use methyl

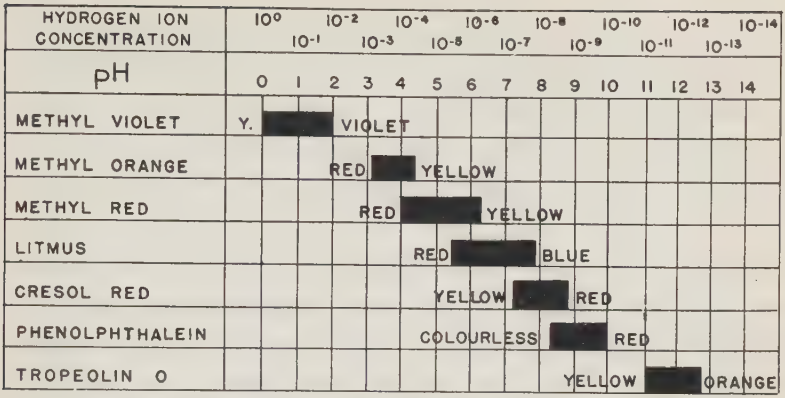


Fig. 126. The colour range of some common indicators.

orange for pH values near to 4, methyl red about 5.5, cresol red about 8 and phenolphthalein for pH values about 9.

5. Hydrolysis. Many salts when dissolved in water not only ionize but the ions disturb the equilibrium between the water and its hydrogen and hydroxyl ions, by using them to reform a little of the acid and base which produced the salt. This process is the reverse of neutralization and is called *hydrolysis*. We usually define hydrolysis as *the action of a salt with water to form an acid and a base*. We may write equations for the reaction of a few salts with water if we remember that the reaction usually does not go very far toward completion.

(i) $NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$

(ii) $K_2CO_3 + 2\ H_2O \rightleftharpoons 2\ KOH + H_2CO_3$

(iii) $(NH_4)_2CO_3 + 2\ H_2O \rightleftharpoons 2\ NH_4OH + H_2CO_3$

(iv) $AlCl_3 + 3\ H_2O \rightleftharpoons Al(OH)_3 + 3\ HCl$

The reverse reaction of neutralization is indicated by a very heavy arrow to show that it is the most rapid reaction, and hydrolysis does not proceed very far until the acid and base neutralize one another as fast as they are formed by hydrolysis.

The action actually takes place between the ions of water and the ions of the salt. For (*i*) above we may indicate the changes as follows:

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$
$$H_2O \rightleftharpoons OH^- + H^+$$
$$\uparrow\downarrow$$
$$NH_4OH$$

If you look at the table of degrees of dissociation in Chap. 24 you will see that NH_4OH is a weak base so it tends to remain undissociated. Any NH_4OH which forms removes OH^- ions and NH_4^+ ions, and leaves an excess of H^+ and Cl^- in the solution. The solution thus becomes acidic and if litmus is placed in a solution of NH_4Cl it turns red. We say that NH_4Cl is *the salt of a weak base and a strong acid* and such a salt *hydrolyzes in water to give an acidic solution.*

For (*ii*) above we may write ionic equilibria:

$$K_2CO_3 \rightleftharpoons 2\ K^+ + CO_3^=$$
$$2\ H_2O \rightleftharpoons 2\ OH^- + 2\ H^+$$
$$\uparrow\downarrow$$
$$H_2CO_3$$

Again the table will show you that H_2CO_3, carbonic acid, is a weak acid so it removes hydrogen ions from the solution and leaves an excess of OH^- ions. Such a solution will be basic to litmus which it will turn blue. The H_2CO_3 will not decompose into water and carbon dioxide because the carbon dioxide is absorbed by the alkaline solution. This is *a salt of a strong base and a weak acid and such a salt hydrolyzes in water to give a basic solution.*

For (*iii*) above we have several ionic equilibria:

$$(NH_4)_2CO_3 \rightleftharpoons 2\ NH_4^+ + CO_3^=$$
$$2\ H_2O \rightleftharpoons 2\ OH^- + 2\ H^+$$
$$\uparrow\downarrow \qquad \uparrow\downarrow$$
$$2\ NH_4OH \qquad H_2CO_3$$

Now both the acid and the base formed by hydrolysis are weakly ionized and use up the ions of the salt and of water. A much larger proportion of the salt will be hydrolyzed and the solution smells strongly of ammonia. This is the reason for the name "smelling salts" given to ammonium carbonate. It reacts with any water present to give off a stimulating odour of ammonia which often cures a tendency to faint. *A salt of a weak acid and a weak base hydrolyzes strongly in water to give an acidic, a neutral or a basic solution according to the relative strength of the acid and base.* In this case the solution is slightly alkaline because ammonium hydroxide is more highly ionized than carbonic acid.

In (*iv*) above we have a new factor tending to increase the degree of hydrolysis. One of the products of hydrolysis is rather insoluble in water and tends to remove ions by forming a precipitate.

$$\begin{array}{l} AlCl_3 \rightarrow Al^{+++} + 3\ Cl^- \\ 3\ H_2O \rightleftarrows 3\ OH^- + 3\ H^+ \\ \qquad\qquad \downarrow \\ \qquad\quad Al(OH)_3 \end{array}$$

The aluminum hydroxide is not soluble unless the pH rises to less than 4; therefore the hydrolysis proceeds until there is enough hydrochloric acid present to dissolve the precipitate. The aluminum hydroxide separates as a gelatinous mass which absorbs many impurities and traps bacteria when it is filtered out. For this reason municipal water supplies are treated with alum (aluminum sulphate) and lime to neutralize the acid and promote the hydrolysis of the salt, before they are filtered. *A salt which hydrolyzes to give an insoluble hydroxide will give an acidic solution.* An insoluble hydroxide has the same effect as a weak base. If the hydroxide is insoluble and the acid is also weak or little soluble the salt will be

completely hydrolyzed in water. For this reason the sulphides of aluminum, calcium and barium among others are not formed in aqueous solutions.

6. Neutralization. The whole story of neutralization can now be told. *When an acid reacts with an equivalent amount of a base to form a salt and water* we call it *neutralization.* In Chap. 24 we learned that water is so little ionized that neutralization reactions run far toward completion but we have just learned that the reverse reaction of hydrolysis keeps the reaction from being 100 per cent complete. We should now classify neutralizations according to the type of salt produced.

Type I. Neutralization of a strong acid with a strong base.

The example could be any pair of the highly ionized acids and bases in Table 20. e.g., NaOH and HCl.

$$\begin{aligned} NaOH &\rightarrow Na^+ + OH^- \\ HCl &\rightarrow Cl^- + H^+ \\ &\quad \downarrow\uparrow \\ &\quad H_2O \end{aligned}$$

Since no weak base, no weak acid, nor any insoluble substance can be formed by hydrolysis this reaction will run essentially to completion and the numbers of hydrogen and hydroxyl ions should be equal. The solution should be neutral when equivalent amounts of acid and base have been added.

Type II. Neutralization of a weak acid with a strong base.

The usual example is acetic acid and sodium hydroxide.

$$\begin{aligned} H.C_2H_3O_2 &\rightleftarrows H^+ + C_2H_3O_2^- \\ NaOH &\rightarrow OH^- + Na^+ \\ &\quad \downarrow\uparrow \\ &\quad H_2O \end{aligned}$$

This reaction yields sodium acetate which hydrolyzes slightly in water to re-form some of the acetic acid which is only

slightly ionized. When equivalent amounts of acetic acid and sodium hydroxide are mixed in water the solution is basic due to hydrolysis. We would use phenolphthalein to indicate the presence of equivalent amounts of acid and base.

Type III. Neutralization of a strong acid with a weak base.

A common case is the use of hydrochloric acid to neutralize ammonium hydroxide solutions.

$$\begin{array}{c} HCl \rightarrow H^+ + Cl^- \\ NH_4OH \rightleftarrows OH^- + NH_4^+ \\ \uparrow\downarrow \\ H_2O \end{array}$$

The reaction proceeds almost to completion because water is so slightly ionized, but the ammonium ions remove the OH^- ions also to remake a little ammonium hydroxide. When equivalent amounts are added the resulting solution is slightly acidic due to the excess hydrogen ions left in the solution. Methyl red is used to indicate when equivalent amounts of these two substances have been added because it changes colour in a slightly acid solution.

Type IV. Neutralization of a weak acid with a weak base.

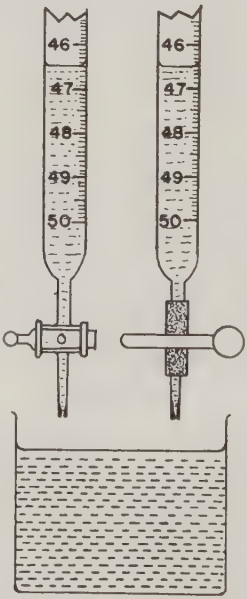
Acetic acid and ammonium hydroxide will illustrate this.

$$\begin{array}{c} H.C_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^- \\ NH_4OH \rightleftarrows OH^- + NH_4^+ \\ \uparrow\downarrow \\ H_2O \end{array}$$

Some of the $NH_4C_2H_3O_2$, ammonium acetate, is never formed because the acid and the base are incompletely ionized and the reaction stops short of completion. Water is so little ionized that most of the hydrogen and hydroxyl ions are removed from the acid and the base, but not all of them. Since the acid and the base are equally weak equiva-

lent amounts of them will give an almost neutral solution. *In every acid-base neutralization the hydrogen ion of the acid combines with the hydroxyl ion of the base to form water and leave the ions of a salt.* From this discussion you can see that equivalent amounts of an acid and a base may not give an exactly neutral solution. It may be necessary to add a little extra of a strong base or acid if exact neutrality is required in neutralizing a weak acid or base.

7. Titration. *The common method for determining the concentration of a solution is to add an equivalent amount* of a solution of known strength. The process is called *titration.* The most used instrument for measuring liquid volumes in titration is a *burette.* It is a long cylindrical glass tube with a stopcock at the bottom followed by a fine tip. It is graduated so that the volume delivered can be determined to the nearest 0.01 ml. The unknown solution is usually placed in one



If 46.5 ml. of 0.5 n. acid is measured into the beaker by this acid burette, then

$\frac{46.5}{1000} \times 0.5 = 0.02375$

Equivalents of acid have been added.

When 46.5 ml. of 0.5 n. base has been added from this base burette then

$\frac{46.5}{1000} \times 0.5 = 0.02375$

Equivalents of base have been added.

Fig. 127. The titration of an acid with a base. Equivalent amounts are required.

burette and the known solution in another. A portion of the unknown is measured out into a beaker or a flask and the known solution added until the two are found to have reacted in equivalent amounts. An indicator is used to determine this point, called the *end point* (see Fig. 127). When the concentration of an acid solution is sought it is titrated with a solution of a base of known concentration. The process is called *acidimetry* which means measuring the total acidity. When the concentration of a basic solution is found by using an acid of known concentration the process is called *alkalimetry*. The proper indicator must be used to show when equivalent amounts have reacted.

8. Calculations of titrations. Normal solutions are most frequently used in titrations because their strength is given in equivalent weights per litre which is the same as milliequivalent weights per millilitre. Titration equipment measures the volume in millilitres so the quantity of each reactant is given by the product of the volume and the concentration. When equivalent quantities have been added we can use the same rule that we used for the dilution of solutions in Chap, 24, sec. 5.

$\text{Volume}_1 \times \text{Concentration}_1 = \text{Volume}_2 \times \text{Concentration}_2$.

Since acids and bases are frequently dealt with

$$\mathbf{V_A \times N_A = V_B \times N_B}$$

where V_A and V_B are the volumes of the acid and the base and N_A and N_B are their normalities.

Example 1. What is the normality of a sodium hydroxide solution if 40 ml. of it are equivalent to 50 ml. of a 0.2 N hydrochloric acid solution?

Solution of problem:

$$50 \times 0.2 = 40 \times N_B$$
$$N_B = \tfrac{50}{40} \times 0.2 = 0.25 \text{ N.}$$

Can you identify N_A, V_A and V_B in the equation?

Example 2. What volume of 0.5 N sulphuric acid is needed to just neutralize 200 ml. of 1.5 N potassium hydroxide?

Solution of problem: An equivalent amount of sulphuric acid is needed to just neutralize the strong base.

Here $V_B = 200$, V_A is unknown, $N_A = 0.5$ and $N_B = 1.5$

$$V_A \times 0.5 = 200 \times 1.5$$
$$V_A = 200 \times \tfrac{1.5}{0.5}$$
$$V_A = 600 \text{ ml.}$$

In finding the strength of the known acid or base the reagent is sometimes weighed out, if it can be obtained pure, and the known quantity dissolved to produce the required volume of solution. We use the relation:

$$V \times N = \text{milliequivalents}$$

Example 3. What is the weight of sodium hydroxide in 40 ml. of 0.5 N solution?

This solution contains 0.5 equivalent weights per litre or 0.5 milliequivalent weights per millilitre. The milliequivalent weight is 1/1000 times the equivalent weight. The equivalent weight of sodium hydroxide is $23 + 16 + 1 = 40$ g. One milliequivalent weight is 0.04 g. The weight of NaOH in 40 ml. $= 40 \times .04 = 1.6$ g.

Since the quantities used in a titration are equivalent we can calculate the weight of a reactant in an unknown volume from the volume of a known solution required to react with it.

Example 4. A flask contains enough sodium hydroxide solution to require 35 ml. of 0.16 N nitric acid for its neutralization. How much NaOH is in the flask? The volume of *acid* times its normality gives the number of milliequivalents of *base* in the flask because there must be equal numbers of each to react completely.

$$35 \times 0.16 = 5.6 \text{ milliequivalents.}$$

The milliequivalent weight of sodium hydroxide is 0.04 g. so the weight in the flask is

$$5.6 \times 0.04 = .224 \text{ g.}$$

9. Precipitation. A saturated solution of an electrolyte is one of the best examples of equilibrium. If the electrolyte is only slightly soluble an ion product constant can be found for it in the same way as for water. It is called a solubility product constant or a K_{sp}. For a substance which gives only *two* ions it is simply

$$\text{Concentration of cation} \times \text{concentration of anion} = K_{sp}.$$

For example, silver chloride is a slightly soluble salt and a litre of water will dissolve enough silver chloride to give

0.00001 (10^{-5}) gram equivalent weights of silver and chloride ions to the solution. Any excess of the silver salt will not dissolve.

$$\text{Solid AgCl} \rightleftarrows \text{Ag}^+ + \text{Cl}^-$$

Solution of silver chloride continues only until silver ion concentration $\times$ chloride ion concentration $= 10^{-10}$.

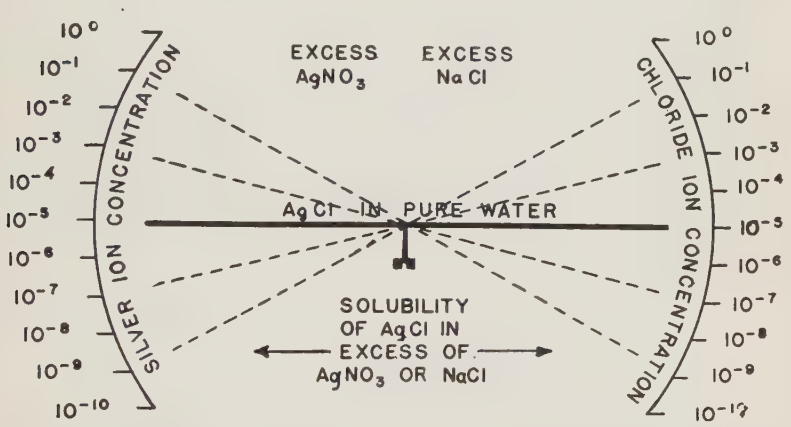


Fig. 128. When the silver ion concentration is increased the chloride ion concentration is decreased so less silver chloride is in solution.

If silver ions in the form of silver nitrate are added to a solution containing chloride ions *a precipitate will commence to form as soon as the product of the concentrations* of the ions exceeds the K_{sp}, 10^{-10}, because at this point the solution is saturated. This is just like the equilibrium between water and its ions. You do not require equal numbers of each kind. If the chloride ion concentration in the water is 0.001 (10^{-3}) gram equivalent weights per litre, then when the silver ion concentration exceeds 10^{-7} gram equivalent weights per litre a white precipitate will start to form. This is the test for a chloride. A little nitric acid is added to prevent the precipitation of other slightly soluble silver salts such as silver carbonate (see Fig. 122).

This principle of precipitation applies to all solutions of electrolytes which have a limited solubility. *When the product of the concentrations of the ions exceeds a certain value the solution is saturated whether or not the numbers of ions of each kind are in equivalent amounts.* The ion which is scarce in the solution gets forced into the solid if there is a large excess of oppositely charged ions to capture it. This is illustrated in Fig. 128.

10. Common-ion effect. The principle that an increase in the concentration of one ion of a slightly soluble substance will cause a decrease in the concentration of its other ion is used to drive substances out of solution by adding an excess of a substance which has a common ion. For example, hydrochloric acid may be used to decrease the solubility of barium chloride in water.

$$BaCl_2 \rightleftarrows Ba^{++} + 2\ Cl^-$$
$$HCl \longrightarrow H^+ + Cl^-$$

The chloride ion is common to the two substances. If we take a saturated solution of barium chloride from above its crystals, place it in a test tube and add some concentrated hydrochloric acid we increase the concentration of the chloride ions, but to restore equilibrium some barium ions will have to leave the solution as barium chloride. The ionization equilibrium is disturbed. It runs in the reverse direction until the product of the concentrations is again equal to its constant value. We might use the Principle of Le Chatelier and say that the addition of the excess chloride ions is a stress on the equilibrium and it tries to relieve the stress by shifting in the direction which removes chloride ions as solid barium chloride. We find it to be a general rule that *the solubility of a slightly soluble substance is decreased by the addition to its solution of a substance having a common ion.*

This common-ion effect is used to control the concentration of sulphide ion in solutions saturated with hydrogen sulphide.

$$H_2S \rightleftarrows 2\,H^+ + S^=$$

Hydrogen sulphide is only slightly soluble in pure water, and if a strong acid is present in the water the presence of the common hydrogen ions reduces the amount of sulphide ion which can remain in equilibrium with it very sharply. This enables us to control the sulphide ion concentration of a saturated solution by regulating the acidity.

Many metals form very slightly soluble sulphides and the careful regulation of the sulphide ion concentration enables us to separate the metal ions by precipitation as described in Chap. 38, sec. 7.

Question Summary

1. What is meant by the term ionic equilibria?

2. (*a*) Would pure water conduct any current?
(*b*) What rule enables us to calculate the number of equivalent weights of hydroxyl ion per litre if we know the equivalent weights of hydrogen ion present in the water?
(*c*) What is a neutral solution? an acidic solution? a basic solution?

3. (*a*) Explain how the pH measures the acidity of a solution.
(*b*) Explain how the pH measures the basicity of a solution.
(*c*) Tell whether the following solutions are acidic or basic: (*i*) pH = 3, (*ii*) pH = 8, (*iii*) pH = 1.4 (*iv*) pH = 10.5.

4. (*a*) Do indicators indicate neutrality? Explain.
(*b*) What indicator would you use to detect pH = 8.5?

5. (*a*) What is hydrolysis? Use equations for examples.
(*b*) Describe carefully the equilibrium shifts which occur when each of the following is dissolved in water: sodium carbonate, cupric nitrate, ammonium acetate, sodium borate.
(*c*) How far would the hydrolysis of sodium chloride proceed? Give your reasons.
(*d*) How far would the hydrolysis of calcium sulphide proceed? Give your reasons.

6. (*a*) Why could the whole story of neutralization not be told before hydrolysis was discussed? Tell it briefly but completely now.

7. What is the meaning of the following terms: titration, burette, end point, equivalent amount, acidimetry, alkalimetry?

8. Why are normal solutions used in titrations?

9. (*a*) How is the equilibrium between a solid and its saturated solution like the equilibrium between water and its ions?

(*b*) When does precipitation occur?

(*c*) Is it necessary to have equal numbers of cations and anions in a solution to cause precipitation?

10. (*a*) Explain what is meant by the common-ion effect.

(*b*) How could you decrease the solubility of a slightly soluble electrolyte in solution?

(*c*) How can the sulphide ion concentration of a saturated hydrogen sulphide solution be regulated?

Problems

1. How would you prepare 500 ml. of 1 N H_2SO_4 by weighing out 98% sulphuric acid?

2. How would you prepare one litre of 1 N NaOH by weighing out lye which analyses 90% NaOH?

3. How many ml. of the solution in **1** above would be required to neutralize 40 ml. of the solution in **2**?

4. Determine the normality of a sulphuric acid solution from the fact that 40 ml. of it exactly neutralized 48 ml. of 0.99 N sodium hydroxide solution.

5. How many ml. of 1 N HCl are required to react with 30 ml. of 1.53 N KOH?

6. 35 ml. of a standard solution of HCl reacted exactly with .224 g. of pure sodium carbonate. What is the normality of the HCl?

7. If 53.3 ml. of 0.5 N NaOH is required to titrate 13.67 ml. of cider vinegar what is the weight of acetic acid per litre in the vinegar?

8. A 50 ml. sample of sodium hydroxide solution required 38 ml. of 0.294 N nitric acid to reach the end point. What is its normality?

9. What is the purity of concentrated sulphuric acid which has a density of 1.80 if 5 ml. of it require 169.2 ml. of 1 N NaOH for complete neutralization?

10. In standardizing a certain base it was found that 25.00 ml. of it were exactly neutralized by 19.98 ml. of a 0.1002 N acid. What is the exact normality of the base?

Chapter **26**

The Colloidal State of Matter

1. Introduction. Lying between the true solution and the coarse suspension (Chap. 21) are mixtures containing one substance dispersed in a fine state of subdivision in another substance. The particles of the dispersed substance are not visible, they do not settle to the bottom and they cannot be separated by filtration. Suspensions of this kind are known as *colloidal suspensions* and the dispersed substance is said to be in the *colloidal state.* The substance in which the particles are dispersed is the *dispersing medium* and the particles themselves constitute the *dispersed phase.* The two substances together form a *colloidal system.* A colloidal dispersion in a liquid is known as a *sol*, and if the liquid is water it is a *hydrosol.* If a sol is coagulated it becomes a *gel* or *jelly.* The difference between a solution, a dispersion and a suspension is illustrated in Fig. 129.

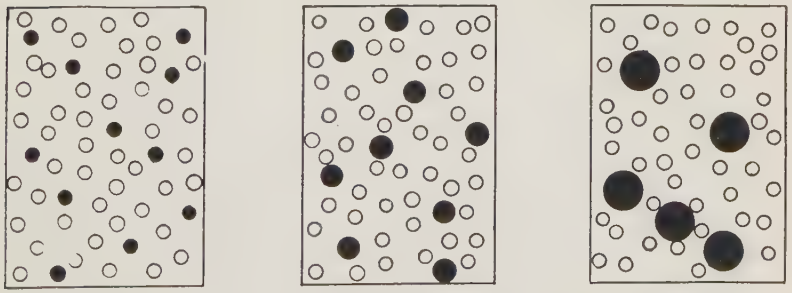


Fig. 129. A colloid is intermediate between a solution and a suspension.

2. The size of the particles. Apparently a colloidal suspension differs from a true solution on the one hand and a suspension on the other by the size of the particles. As the particles are very small it is necessary to employ small units of measurement for their diameters. The units employed are the *micron* and the *millimicron*. The micron is 0.001 mm. and is designated by the Greek letter μ (mu). The millimicron is 0.001 μ, or 0.000001 mm. and is designated by $\mu\mu$ (mu mu). In some texts $\mu\mu$ is written as mμ (milli-mu).

The following table shows the size of particles in various types of mixtures:

TABLE 21—DIAMETERS OF DISPERSED PHASE

Solutions	Less than 1.0 $\mu\mu$.
Colloidal suspensions	From 1.0 $\mu\mu$. to 0.1 μ.
Suspensions	Greater than 0.1 μ.

3. The colloidal state. In 1861 Thomas Graham was investigating the passage of liquids through animal membranes. He found that substances like sugar and various salts would pass through membranes, but that substances like starch, glue, or gum would not pass. He named the substances which would pass through, *crystalloids*, and those which would not pass through, *colloids*. For some time it was believed that the colloids represented a distinct group of substances, but it is now realized that the so-called colloidal state is only a matter of the size of the particles of the substance and that all substances can exist in that state under suitable conditions. Sodium chloride does not form a colloidal suspension in water, but if it is formed in a liquid in which *it does not dissolve* it can be produced in the colloidal state. In forming the colloidal state there is the limitation, that a substance cannot be dispersed as a colloid in a substance in which it is soluble. Except for this limitation the colloidal state is merely a question of the size of the particles.

4. The Tyndall effect. You may have noticed that when a beam of sunlight passes through a darkened room, small motes of dust can be seen moving rapidly in the beam. The small dust particles scatter the light at right angles to the beam, and become visible as a patch of light. Their motion is due to the action of convection currents of air. In a similar fashion a beam of light will show the presence of suspended particles in a liquid. This is shown in Figs. 130 and 131, where a beam of light is shown passing through a true solution and a colloidal suspension. When viewed from the side the beam of light is not visible as it passes through the true solution. When the beam passes through the colloidal dispersion its path can be seen clearly. The scattering of a beam of light by particles suspended in a liquid is known as the *Tyndall effect*. It can be used to distinguish between a true solution and a colloidal dispersion.

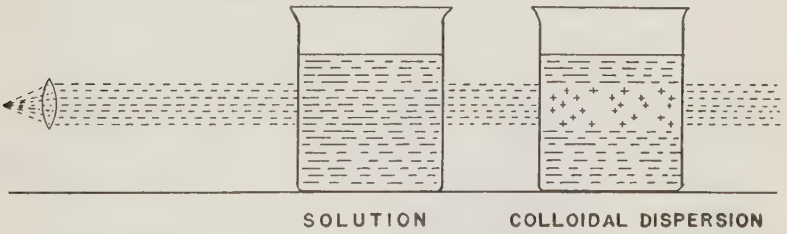
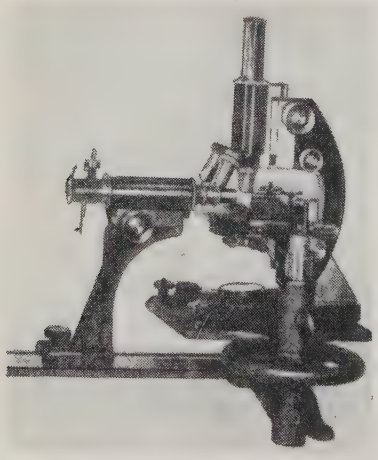


Fig. 130. A true solution has no particles large enough to scatter light.

5. The ultramicroscope. The Tyndall effect is used in the operation of the *ultramicroscope*. In this instrument the liquid to be examined is placed in a glass cell on the stage of the microscope. A beam of brilliant light is focused on the solution so the beam passes through the sides of the glass cell. Any particles suspended in the liquid will scatter the light and will appear as bright discs of light on a dark background. In transmitted light the particles would not be any more visible than the stars in the daytime. While the particle

itself cannot be seen, but only the scattered light from it, it is possible to get some idea of the shape and size of the particle. Colloidal gold particles with a diameter of about 1.7 $\mu\mu$ have been observed.

6. The Brownian movement. One property of a colloidal dispersion is that the particles do not settle even after a long time. Some old samples have not settled after the lapse of one hundred years. Since the particles are heavier than the particles of the dispersing medium, it would be expected that they would settle in a short time. It has been suggested that electrical charges on the particles may cause a repulsion which keeps them in motion, but it has been shown that this effect is not strong enough to account for the lack of settling. The answer is found in the discovery made in 1827 by Robert Brown, an English botanist, and called after him the *Brownian movement*. Brown was making a microscopic study of some grains of pollen which were suspended in water and he noticed that the grains kept up a



Courtesy of Bausch & Lomb Optical Co.

Fig. 131. In the ultramicroscope colloidal particles are revealed by the light they scatter.

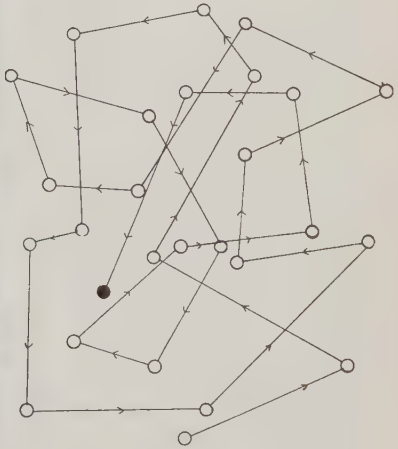


Fig. 132. Successive positions of a particle in Brownian movement.

rapid and erratic movement (see Fig. 132). This movement was studied and it was found that it was not due to convection currents in the liquid or to vibrations from without. The Brownian movement is explained by the striking of the suspended particles by the molecules of the dispersing medium. This bombardment is going on continually, but every now and then chance causes a greater number of molecules to be on one side than on the other and to thus produce a greater thrust in one direction. The variations in the distribution of the molecules and their velocities will cause the suspended particle to move in an erratic path and will prevent it from settling. Colloidal dispersions have been discovered in rocks, where they have been sealed for thousands or even millions of years, and the Brownian movement is seen to be going on as if the systems had been prepared only recently. The Brownian movement exhibits the most striking evidence for the validity of the Kinetic-Molecular Theory.

7. Types of colloidal dispersions. Colloidal systems in which the dispersing medium is a liquid are the most common but others are known. Table 14 shows the possible mixtures and gives a common example of each (see Chap. 21, sec. 4). Substances which form colloidal dispersions in a liquid may be *lyophilic* (liking the liquid) or *lyophobic* (hating the liquid). If the liquid is water, these names become *hydrophilic* and *hydrophobic*.

8. Colloids which like the liquid. These colloids form colloidal dispersions in a liquid without any special methods of preparation. They include substances such as gums, glue, starch, and proteins like gelatin or albumin. They are essentially the substances which Graham designated as colloids These substances show an attraction for the liquid in which they are dispersed and they combine with it in a manner similar to that shown by a hydrate. In fact their name

denotes "attraction by a liquid". A substance which combines with a liquid in that manner is said to be *solvated*. If the liquid is water, as it usually is, they are *hydrated*. Many of these colloids, such as proteins, consist of large complex molecules with high molecular weights. In some of these colloidal systems the disperse phase may consist just of the large molecules themselves. These colloids are *reversible*, that is, if they are precipitated from the dispersed state they will return to that state when placed in the dispersing medium. Albumin may be precipitated from a dispersion in water by the addition of a concentrated salt solution. If the precipitated albumin is washed free from salt and then placed in water it will become redispersed immediately.

9. Colloids which hate the liquid. These colloids are usually insoluble inorganic substances and with them special methods must be employed to produce a colloidal system. They are essentially the substances which Graham designated as crystalloids, and, in order to obtain them in the colloidal state, they cannot be soluble in the dispersing medium. They are not hydrated in water or solvated in the dispersing medium if it is other than water. They are not reversible and, when precipitated, they are not redispersed by the addition of the liquid. A metallic sol, such as colloidal gold in water, is a good example of one of these colloids.

10. The preparation of dispersions. We have seen that some colloids can be dispersed by placing them in the dispersing medium, but that other dispersions require special methods of preparation. Colloidal dispersions represent an intermediate stage between the large particles of a suspension and the molecules of a true solution and depend only upon the size of the particles. This particle size may be obtained either by breaking up a larger particle, or by combining small particles into larger ones. The colloidal state can be produced by either of these methods.

A. Dispersion Methods.

(1) *Mechanical methods.* Solids can be broken up into fine particles by purely physical means, such as grinding. A machine designed to produce this fine state of subdivision is known as a *colloidal mill* and is used in many industries.

(2) *Peptization.* Sometimes the addition of another substance to the dispersing medium will cause the suspended material to break up into finer particles. This process is called *peptization* and the substance which brings it about is known as a *peptizing agent.* Sodium hydroxide acts as a peptizing agent in the preparation of the colloidal dispersion of silicic acid known as water glass. In the case of colloids which are attracted to it, the liquid may be considered to be acting as a peptizing agent.

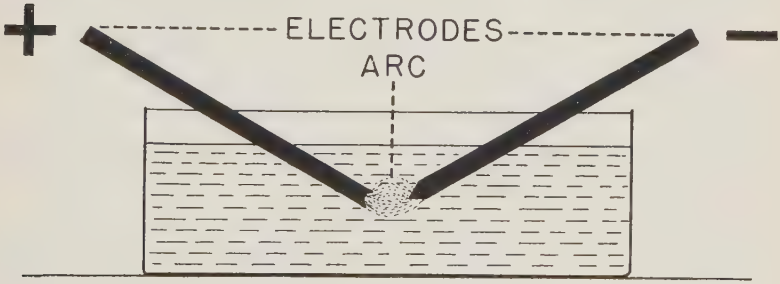
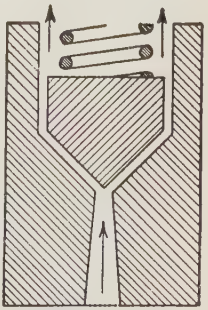


Fig. 133.

Fig. 133. Making a metallic colloid.

Fig. 134. Homogenizer for reducing the size of droplets in emulsions.

(3) *Electrical methods.* Colloidal dispersions of metals in water may be made by the *Bredig arc process* which is shown in Fig. 133. Wires from the current supply lead to two electrodes made of the appropriate metal, touched together under the surface of the water and then separated. The resulting electric arc causes particles



From Holmes: "General Chemistry", courtesy of The Macmillan Company

Fig. 134.

of colloidal dimensions to split off and become dispersed in the water. The metals dispersed in this way must lie below hydrogen in the electro-chemical series. Metals above hydrogen may be dispersed in liquids other than water.

B. Condensation Methods.

These methods depend upon the production of particles of colloidal dimensions by the combining of individual molecules of insoluble substances. These substances are produced in the liquid by either double decomposition or by reduction reactions.

(1) *Double decomposition.* The molecules of certain insoluble substances will coalesce and form larger particles, but if a colloidal dispersion is to be produced, this process must cease before the formation of particles of a size large enough to settle as a precipitate on the bottom of the vessel. A colloidal dispersion of arsenious sulphide may be prepared by this method. If hydrogen sulphide gas is passed into a solution of arsenious oxide in water, the molecules of the resulting arsenious sulphide will coalesce and form particles of colloidal dimensions.

(2) *Reduction.* This method is of historic interest as it was used by Faraday in the production of gold sols. If a few drops of tannic acid are added to a very dilute solution of gold chloride and the solution heated, the gold chloride will be reduced to metallic gold. The molecules of gold will coalesce to form particles of colloidal dimensions. By varying the conditions particles of various sizes may be produced. The colour of the dispersion will vary with the size of the particles. Colloidal dispersions of different metals may be produced by this method and various reducing agents may be employed.

11. Dialysis. In order to remove electrolytes from colloidal dispersions advantage is taken of the fact that the former will pass through certain membranes while the colloids will

not. Substances in the colloidal state will pass through filter paper but will be retained by animal membranes, parchment paper and cellophane. This process is known as *dialysis* and is illustrated in Fig. 135. The colloidal dispersion containing the electrolyte is placed in the upper vessel which is fitted with a suitable membrane. Pure water is circulated through the lower vessel. The electrolyte passes through the membrane and is removed by the circulating water.

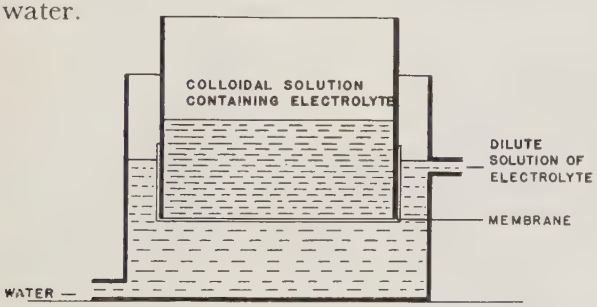


Fig. 135. Colloids may be separated from soluble electrolytes by dialysis.

12. Electrical charges on the particles. In general, colloids possess an electrical charge. If a colloidal dispersion of arsenious sulphide is tested with electrodes, it will be found that it is a conductor and that the colloidal particles will all move towards the positive electrode, showing that they all possess a negative charge. When the particles reach the positive electrode they will lose their charge and coagulate to form a precipitate. These charges are due to the adsorption of ions from the dispersing medium by the particles, and the ions are often hydrogen or hydroxyl ions. Most metallic sulphides possess a negative charge, while metallic hydroxides carry a positive charge. It is the charge of the absorbed ions which causes the particles to move towards the electrode. Since the charges are all alike the particles will repel one another and will not coalesce into larger masses which would settle to the bottom. The charge on the particles is one factor which will prevent the settling of a colloidal dispersion.

In the case of hydrophylic colloids the charge will depend upon the hydrogen ion concentration of the medium. In an acid medium the particles will adsorb hydrogen ions and will acquire a positive charge. In an alkaline medium they will adsorb hydroxyl ions and possess a negative charge. At a certain hydrogen ion concentration the particles will have no charge, and this condition is known as the *iso-electric point* of the system.

13. The effect of electrolytes on colloidal systems. If the electrical charge on the particles is removed the particles will coalesce and precipitate. This process is known as *coagulation*. The presence of large concentrations of ions in a colloidal dispersion will attract the ions of opposite sign which have been adsorbed by the colloidal particle. This attraction between the ions will decrease or remove the charge carried by the particles and will cause coagulation. In the case of arsenious sulphide, we have seen that the particles carry a negative charge due to the adsorption of hydroxyl ions. The presence of much acid will neutralize these particles and will cause a precipitate to form. In general, colloidal dispersions are produced in solutions containing a low ion concentration and are precipitated in solutions with a high ion concentration.

14. Electrical precipitation. We have seen that a colloidal dispersion of arsenious sulphide can be precipitated at the positive electrode. Particles of smoke, which is a dispersion of a solid in a gas, are electrically charged and may be precipitated by passing smoke through a chamber containing electrically charged wires. This is the principle of the *Cottrell precipitator*, which is shown in Figs. 136 and 137. An electrical potential is maintained between the wires and the casing, and when the smoke passes through, the charges on the particles are neutralized and precipitation takes place. This process can be used to prevent smoke nuisance and to

collect dust from various industrial processes. In some cases valuable substances have been recovered from the dust, such as potassium compounds from the dust from cement kilns. Besides removing a nuisance an electrical precipitator will in some cases pay for itself through the recovery of valuable by-products.

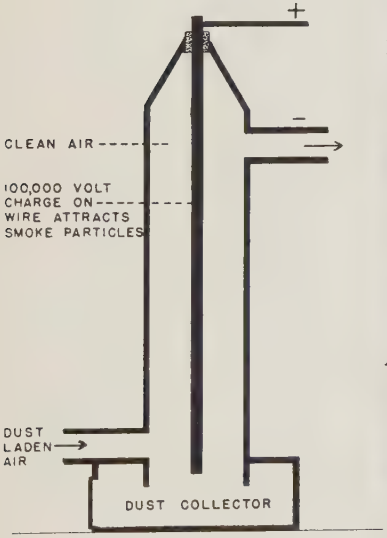
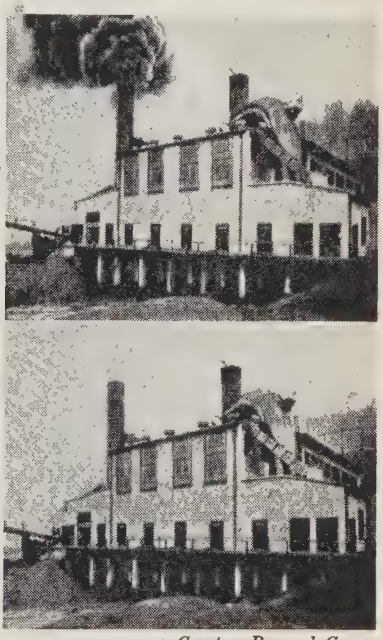


Fig. 136.



Courtesy Research Corp.

Fig. 137.

Fig. 136. The Cottrell precipitator.

Fig. 137. A factory, A, with the current on, and B, off, the Cottrell precipitators.

15. Protective colloids. When two colloids are present in the same system, one may prevent the coagulation of the other. Apparently one of the colloids forms a coating or film around the particles of the other, thus preventing them from coalescing to form larger particles. A substance which thus forms a protecting film is said to be a *protective colloid.* Gelatin is frequently used as a protective colloid. If a solu-

tion of silver nitrate contains a small amount of gelatin it will not precipitate silver bromide from a solution of a bromide. In the preparation of photographic emulsions gelatin is used to protect the colloidal dispersion of silver salts. In the preparation of ice cream gelatin is added to prevent the formation of crystals of sugar and ice. Gum arabic is used as a protective colloid in the manufacture of inks.

16. Emulsions. If we shake a mixture of kerosene and water we obtain a milky fluid which consists of many fine drops of oil dispersed in the water. Such a mixture is known as an *emulsion*. An emulsion prepared in this way is not stable but will separate into two liquid layers with the lighter liquid on the top. To obtain a more permanent emulsion we must add a third substance which is insoluble in both liquids and will migrate to the boundary between them. This substance is known as an *emulsifying agent*. Milk is a stable emulsion in which casein is the emulsifying agent. When milk becomes sour the production of lactic acid precipitates the emulsifying agent, thus causing the emulsion to become unstable. Butter is an emulsion of water in butter-fat. Mayonnaise is an emulsion of oil in vinegar with egg yolk as the emulsifying agent. The cleansing action of soap is due to its power to act as an emulsifying agent in forming emulsions of oil and grease with water. The formation of these emulsions loosens the particles of oily dirt, which may then be washed away. As in the case of the souring of milk, an emulsion may be destroyed by the addition of substances which affect the emulsifying agent. An emulsion of oil and water, in which soap is the emulsifying agent, may be broken up by the addition of an acid which converts the soap into a free fatty acid.

17. Gels. Many hydrophylic colloids coagulate to form *gels* or *jellies*. These gels are cellular substances in which the walls of the cells are composed of strings of united particles. The liquid is contained in the cells as water is held in a sponge.

If acid is added to a solution of sodium silicate, a gel of silicic acid is produced. When this gel is partially dehydrated *silica gel* is produced. This substance has important uses because of its high adsorbent properties. Fruit jellies are made from the acid fruit juice and *pectin*, which is a natural constituent of most fruits and which is obtained in large quantities from apples. The acid causes the hydration of the pectin and the resulting formation of a gel. Gelatine desserts, photographic emulsions, and solid alcohol, are well-known examples of gels. Seeds contain colloidal material which swells when hydrated in the ground and bursts the seed casing.

18. Adsorption. Many substances possess *the property of attracting other substances to their surfaces, where the attracted substance adheres in layers* of a thickness of one molecule. This process is known as *adsorption*. It must not be confused with *absorption*, where one substance penetrates beneath the surface of another as a blotter takes up ink.

If you have a cube which has a side of 1 cm., the total area will be 6 sq. cm. If this cube be divided into 1000 small cubes, each with a side of 0.1 cm., the area of each cube will be 0.06 sq. cm. and the total area of all the cubes will be 0.06×1000 or 60 sq. cm. Thus increasing the subdivision of a substance increases the surface. Since adsorption takes place on the surface the adsorbing power of a substance is increased by dividing it more finely. As particles of colloidal dimensions are very small and are present in large numbers, they must possess a large total surface and have great powers of adsorption.

Colloidal systems are used extensively because of their adsorbing power. Colloidal metallic hydroxides adsorb dyes and act as mordants in dyeing. Finely divided carbon, such as boneblack or powdered charcoal, is used as a decolorizer for sugar solutions.

19. Applications of colloidal dispersions. Colloidal dispersions appear so widely in nature and have so many industrial uses that it is impossible to do more than mention a few of their applications. Most of the constituents of plants and animals are in the colloidal state and many biological processes, such as digestion and secretion, depend upon the existence of a colloidal system. The decomposition of the rocky materials in the soil provides hydroxides of aluminum, iron and silica, which form a colloidal film around particles of clay. This colloidal coating gives clay its plasticity. In Biblical days the Israelites found that they could not make bricks without straw. The aqueous extract of the straw provided a colloidal film for the particles of the clay and made the mass more plastic. Colloidal films around soil particles play an important role in agriculture. They adsorb soluble salts which would otherwise be washed away by rain-water and hold them in readiness for use as plant food. They also provide a bed for the bacteria which are necessary for plant life.

In the purification of water colloids play an important part. Surface waters are polluted with clay and colloidal substances which give a negative charge to the particles of clay. Swamp waters usually contain positively charged organic particles. When these waters are mixed coagulation occurs and the impurities precipitate. Water may be purified by adding ferric or aluminum salts which produce hydroxides on hydrolysis (see Chap. 25, sec. 5). The hydroxides are colloidal and positively charged, so that they attract the negatively charged particles of clay and adsorb colouring matter. The precipitated material is filtered out and the colloidal mass on the filter acts as a trap for bacteria and other organisms. The objectionable portion of sewage usually consists of colloidal nitrogenous material. If the sewage is filtered through crushed stone and sand covered with a colloidal

growth of bacteria, the resulting filtrate will be a harmless liquid.

Colloidal systems play a great part in many industries. The fibres of most textiles are colloidal and so are the particles of the dye. Adsorption causes the dye to adhere to the textile material. If the fibre and the dye are of similar charge a mordant such as aluminum hydroxide may be used. The mordant will neutralize the charge on the fibre so that it can adsorb the particles of the dye. The tanning of leather is also a matter of colloidal particles and adsorption. Plastic substances like rubber, cements, glues, plasters, starches are all in the colloidal state and, in many instances, the setting of these materials involves the formation of a gel. Gums, resins, shellacs and their derivatives are all colloidal in character. Many medicinal substances are produced in the colloidal state, not only to improve the taste, but to make them more available to the human body. We are all familiar with an emulsion of cod-liver oil, which is much more pleasant to take than the oil itself.

Question Summary

1. (*a*) What is the difference in the properties of a solution and a suspension?
(*b*) Define: colloidal suspension, dispersed phase, sol.

2. What are the approximate sizes of the particles in a true solution and in a colloidal suspension?

3. (*a*) What did Graham mean by "colloids" and "crystalloids"?
(*b*) What determines the existence of the colloid state? What limitation is there for its existence?

4. Explain the Tyndall effect in a colloidal suspension.

5. Explain the operation of the ultramicroscope.

6. Explain the Brownian movement.

7. Can you give other examples of different types of dispersions than are in Table 14, (Chap. 21, sec. 4)?

8. (*a*) What are lyophilic colloids? Give examples.
(*b*) What is meant by saying that a colloid is reversible?

9. What is meant by a lyophobic colloid? Give examples.

10. (*a*) Explain how lyophobic dispersions can be produced by mechanical means.
(*b*) What is meant by peptization?
(*c*) Explain the Bredig arc process.
(*d*) How might you produce a colloid by double decomposition?
(*e*) How do you produce colloidal dispersions by reduction?

11. Explain dialysis.

12. (*a*) Explain the effect of electric charges on the particles.
(*b*) What is the iso-electric point of a colloidal system.

13. What is the effect of electrolytes on colloidal suspensions?

14. Explain the operation of an electric precipitator.

15. Explain the action of protective colloids.

16. What is an emulsion? Give examples.

17. What are gels? Give examples.

18. (*a*) What is the difference between "absorption" and "adsorption"?
(*b*) Explain why colloidal systems are used extensively because of their adsorbing power.

19. (*a*) Give examples of the use of colloidal systems in nature.
(*b*) Give examples of the use of colloidal systems in industry.

Topic Five

THE FAMILY TREE

The idea that the elements are related to one another like the grandchildren of a man who has many married sons has always had a great fascination for chemists. Aristotle thought the elements were only qualities impressed upon a basic substance, and in 1815 Prout suggested that all the atomic weights were multiples of hydrogen. Men soon grouped the elements into triads and finally a classification into families was devised. These families were arranged into the periodic table. Across this table the properties of the elements ebbed and flowed like the tides. The relationship may also be shown by the family tree on the next page where the properties change slowly along each branch.

We shall first tell you about two typical families of elements: the very active non-metals (Group VII) and the active metals (Group I) found on either side of the tree. It will make your study of chemistry much easier if you learn the characteristics of a group of elements and then learn resemblances and differences between the elements. The family tree will help you to do this.

Drawn by W. S. A. Singh

The Family Tree of the Elements

Chapter 27

Chlorine and Hydrochloric Acid

1. Introduction. Besides air and water, common salt is the best known chemical. Salt was prepared from brine or sea-water from the earliest times because it is a vital constituent of the food of men and animals. In 1648 Glauber obtained a strongly acid substance by heating wet salt on a charcoal burner. He called it "spirit of salt". Ten years later he found it could be produced in large quantities by warming salt with sulphuric acid. Priestley found that "spirit of salt" or marine acid air, as he called it, was a permanent gas and could only be collected over mercury. Its solution in water was called marine acid or muriatic acid from the word *muria* meaning brine. We now call it hydrochloric acid.

In 1774 Scheele heated the acid with manganese dioxide and obtained a greenish-yellow gas. He was thus the discoverer of chlorine. In 1810 Davy heated charcoal, sulphur, phosphorus and many metals in chlorine but could find no oxygen compounds so he declared it to be an element.

CHLORINE

2. Occurrence. Chlorine is a very active element and is therefore not found in the free state. Its compounds are well known, the most important being sodium chloride, found in sea-water and in deposits in the earth. These deposits of sodium chloride contain other salts, such as the chlorides of potassium, calcium and magnesium, and were laid down by the evaporation of inland seas many years ago. Very

famous deposits are found at Stassfurt in Germany where the salt is mined for the potassium chloride which is valuable as a fertilizer. There are important salt deposits in Nova Scotia, Ontario and Saskatchewan. Most of the chlorine compounds found in nature are quite soluble in water, but one insoluble silver compound, silver chloride, known as *horn silver*, is mined as a silver ore.

3. The preparation of chlorine.

A. Laboratory methods.

(1) *By heating manganese dioxide with hydrochloric acid.* Chlorine may be prepared by oxidizing hydrochloric acid. The most common laboratory method consists in placing manganese dioxide in a flask to which some hydrochloric acid is added. On heating the flask chlorine will be evolved. The apparatus is shown in Fig. 138. As the gas is soluble in water it cannot

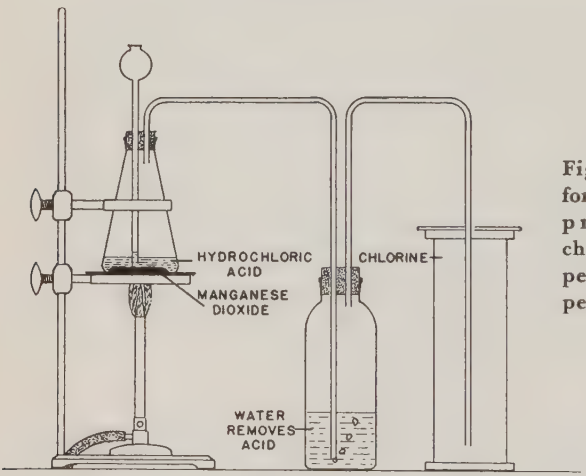


Fig. 138. Apparatus for the laboratory preparation of chlorine. This experiment should be performed in a hood.

be collected in a pneumatic trough over water, but being heavier than air it may be collected by the upward displacement of air as shown. The wash bottle shown in the figure contains water to trap any hydrochloric acid that may be carried over with the chlorine. During this experiment great

care must be taken not to breathe the gas as it is unpleasant and poisonous. In this reaction the hydrochloric acid reacts with the manganese dioxide to produce manganese tetrachloride and water.

$$4\ HCl + MnO_2 \longrightarrow MnCl_4 + 2\ H_2O$$

The tetrachloride is very unstable and it breaks up into manganous chloride and free chlorine which is given off.

$$MnCl_4 \longrightarrow MnCl_2 + Cl_2$$

By cancelling out the $MnCl_4$, which is common to both, the equations may be combined in one as follows:

$$4\ HCl + MnO_2 \longrightarrow MnCl_2 + 2\ H_2O + Cl_2$$

It will be noticed that half of the chlorine in the hydrochloric acid is given off as chlorine gas. In manganese tetrachloride the manganese has a valence of 4, while in manganous chloride it has a valence of 2. While the hydrochloric acid is oxidized the manganese is reduced, so this is an example of an oxidation-reduction reaction.

(2) *By the action of hydrochloric acid on potassium permanganate.* If crystals of potassium permanganate are placed in a flask and concentrated hydrochloric acid be allowed to drop upon them, chlorine will be given off and may be collected in the usual manner. By the use of a dropping funnel the action of the acid may be controlled. This is a convenient method of obtaining small quantities of chlorine as the evolution of the gas may be controlled easily and no heat is required. The equation for this reaction is as follows:

$$2\ KMnO_4 + 16\ HCl \longrightarrow 2\ KCl + 2\ MnCl_2 + 8\ H_2O + 5\ Cl_2$$

It will be noticed that more than half of the chlorine in the acid is obtained by this method.

(3) *By the action of manganese dioxide, sodium chloride and sulphuric acid.* If a mixture of manganese dioxide, sodium

chloride and sulphuric acid is heated chlorine is given off. In this reaction the sodium chloride and sulphuric acid react to form hydrochloric acid.

$$2\ NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ HCl$$

The manganese dioxide and sulphuric acid react to produce manganese sulphate, water and nascent oxygen.

$$MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + (O)$$

You will recall that atomic oxygen is produced when there is a substance present which will react with it, and in this case it oxidizes the hydrochloric acid to produce chlorine.

$$(O) + 2\ HCl \longrightarrow H_2O + Cl_2$$

These equations may be combined to produce one equation as follows:

$$2\,NaCl + 2\,H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + 2\,H_2O + Cl_2$$

Notice that all of the chlorine present in the sodium chloride is obtained as free chlorine.

B. Industrial method.

The electrolysis of a solution of sodium chloride. A solution of sodium chloride will contain ions from both the salt and the water.

$$NaCl \rightleftarrows Na^+ + Cl^-$$
$$H_2O \rightleftarrows H^+ + OH^-$$

When the electrodes are charged by the applied voltage the positive ions migrate to the cathode and the negative ions migrate to the anode as shown in Fig. 139. Nature follows the path of least resistance in the discharge of these ions and the hydrogen ions are very much easier to discharge than the sodium ions, so hydrogen gas is evolved at the cathode instead of sodium.

In a concentrated solution of sodium chloride the chloride ions are actually easier to discharge than the hydroxyl ions

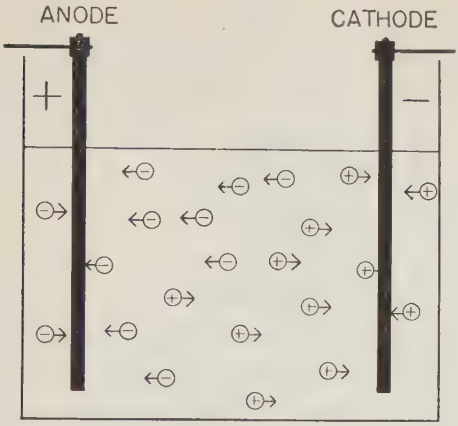


Fig. 139. Electrolysis of brine. Chlorine is collected at the anode and hydrogen at the cathode.

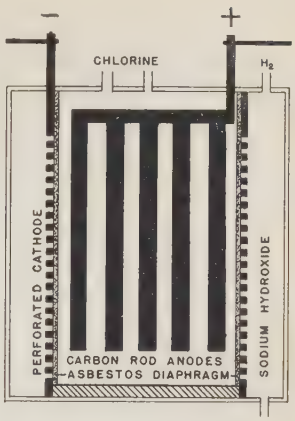


Fig. 140. Diagram of a Nelson cell.

although the reverse is true in dilute solution. Thus chlorine is produced at the anode of the cell. This leaves sodium ions and hydroxyl ions in the solution. Sodium hydroxide may be obtained from this solution. The over-all reaction is

$$2\ NaCl + 2\ H_2O \longrightarrow 2\ NaOH + H_2 + Cl_2$$

Commercial cells are designed to effect the separation and removal of the products as shown in Fig. 140. In this cell the anode consists of a group of carbon rods immersed in the brine. Around the anode is a circular cathode of sheet steel which is separated from the brine by an asbestos diaphragm. The sodium hydroxide collects in the space outside of the diaphragm and may be drawn off. This method serves as a means of obtaining chlorine, hydrogen and sodium hydroxide and is a valuable industrial process.

4. The physical properties of chlorine. Chlorine is a greenish-yellow gas with an irritating odour. It dissolves slightly in water to give *chlorine water*. It is about two and one half times as dense as air.

5. The chemical properties of chlorine. Dry chlorine does not appear to attack metals and the gas may be shipped in steel cylinders and tank cars, but a trace of moisture causes a vigorous action even with the less active metals. In all cases the chlorides of the metals are formed.

$$2\ Fe + 3\ Cl_2 \longrightarrow 2\ FeCl_3$$
$$Cu + Cl_2 \longrightarrow CuCl_2$$
$$2\ Au + 3\ Cl_2 \longrightarrow 2\ AuCl_3$$

Chlorine combines with most of the non-metals except fluorine but combines only indirectly with oxygen and nitrogen. With phosphorus it forms the liquid trichloride, PCl_3, and, with an excess of chlorine, the solid pentachloride, PCl_5. When dry hydrogen and chlorine are mixed together in the dark they do not combine, but if the mixture is exposed to sunlight or to a photographic flash light they combine explosively to form hydrogen chloride.

$$H_2 + Cl_2 \longrightarrow 2\ HCl$$

A jet of burning hydrogen continues to burn when it is lowered into a jar of chlorine. Heat and light are given off and the reaction resembles the burning of hydrogen in oxygen, except that hydrogen chloride is produced instead of water. This is an example of combustion without oxygen. Chlorine has such an affinity for hydrogen that it will remove it from its compounds. When a burning candle is lowered into a jar of chlorine it will burn with a smoky flame since the chlorine combines with the hydrogen in the gas from the candle leaving the carbon. This affinity for hydrogen is shown strikingly when a piece of filter paper is soaked in turpentine and placed in a jar of chlorine. Turpentine is a hydrocarbon, $C_{10}H_{16}$, and the hydrogen is taken by the chlorine to form hydrogen chloride while the carbon is left and forms a dense black smoke.

$$C_{10}H_{16} + 8\ Cl_2 \longrightarrow 16\ HCl + 10\ C$$

Chlorine is a more active element than bromine, iodine and sulphur, so it will displace these elements from their compounds.

$$2\ NaBr + Cl_2 \longrightarrow 2\ NaCl + Br_2$$
$$2\ NaI + Cl_2 \longrightarrow 2\ NaCl + I_2$$
$$H_2S + Cl_2 \longrightarrow 2\ HCl + S$$

The displacement of iodine from its compounds and the production of free iodine is used as a test for chlorine. In this test filter paper is soaked with a solution of potassium iodide and starch. In the presence of chlorine this paper will turn blue due to the action on the starch of the iodine which is liberated by the chlorine.

Chlorine also forms addition compounds with certain substances. As mentioned in the chapter on carbon, chlorine forms carbonyl chloride, or phosgene, $COCl_2$, with carbon monoxide. Chlorine hydrate, $Cl_2.8H_2O$, is formed as yellowish-green crystals when ice water is saturated with chlorine. We have seen how some oxides combine with additional oxygen, e.g., cuprous oxide, Cu_2O, is oxidized to cupric oxide, CuO. In a similar manner chlorine will add to substances which already contain chlorine and we have

$$2\ CuCl + Cl_2 \longrightarrow 2\ CuCl_2$$
$$2\ FeCl_2 + Cl_2 \longrightarrow 2\ FeCl_3$$
$$2\ HgCl + Cl_2 \longrightarrow 2\ HgCl_2$$
$$SnCl_2 + Cl_2 \longrightarrow SnCl_4$$

In these reactions the valence of the metal is increased, so they are oxidation reactions.

When chlorine is dissolved in water it reacts with the water to form hydrochloric and hypochlorous acids.

$$Cl_2 + H_2O \longrightarrow HCl + HClO$$

Hypochlorous acid is unstable and will decompose to yield hydrochloric acid and oxygen. The oxygen is given off

in the atomic form which, you will recall, is readily available if a substance is present to be oxidized.

$$HClO \longrightarrow HCl + (O)$$

In the presence of sunlight bubbles of oxygen will be given off from chlorine water and hydrochloric acid will be produced.

$$2\ HClO \longrightarrow 2\ HCl + O_2$$

6. The uses of chlorine. Chlorine is used largely in bleaching and disinfecting. It is used as a bleaching agent for textiles and wood pulp. For this purpose it is usually used in the form of "bleaching powder" which is a double salt of calcium with hydrochloric and hypochlorous acids, $CaOCl_2$. The bleaching action of chlorine depends on the oxidizing action of the hypochlorous acid obtained by the action of an acid on bleaching powder or from a solution of chlorine in water. In bleaching, the dye is oxidized to a colourless substance and it must be noted that it is the oxygen produced by the action of the chlorine, rather than the

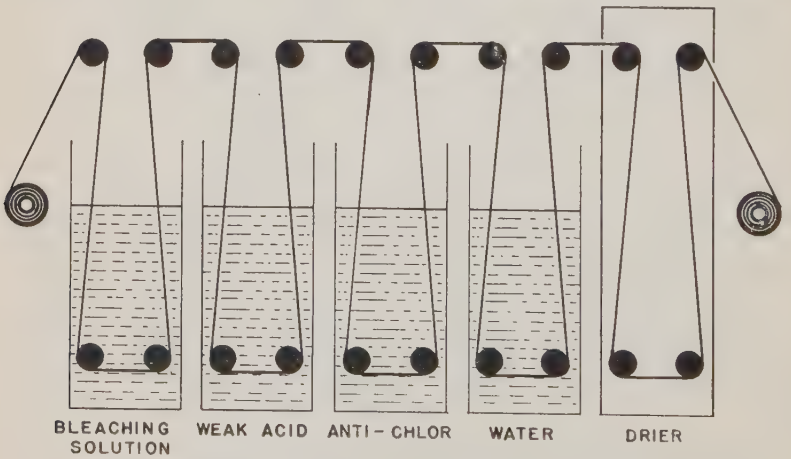


Fig. 141. Diagram of commercial process of bleaching cotton goods.

chlorine itself, which performs the bleaching action. In the bleaching of textiles the material is run through a bath of bleaching powder solution, then into a weak acid and then through a bath of a substance known as an *anti-chlor*, to remove the chlorine which might weaken the fabric if allowed to remain. Sodium sulphite, Na_2SO_3, is frequently used as an anti-chlor. After passing through the anti-chlor the material is run through a bath of water and finally dried and ironed. This process is shown diagrammatically in Fig. 141.

The use of chlorine as a disinfectant depends also upon the production of oxygen, which oxidizes the bacteria. The presence of a small amount of chlorine in water is sufficient to destroy all dangerous micro-organisms and liquid chlorine supplied in cylinders is used generally for this purpose. Almost all municipal water supplies depend on the use of chlorine for their disinfecting and the gas is often used in swimming pools. This use of chlorine has contributed greatly to the health of the world in preventing epidemics of diseases such as typhoid and dysentery.

When a solution of sodium carbonate is treated with chlorine a solution containing sodium hypochlorite and sodium chloride is obtained. This solution is used as a germicide under various trade names and was developed as Carrel-Dakin solution during World War I.

Chlorine is used for the recovery of tin from waste metal from the manufacture of tin cans. When this metal, consisting of sheet iron covered with tin, is treated with chlorine, stannic chloride, $SnCl_4$, is produced, from which the tin may be recovered. Chlorine will also react with gold in its ores to form auric chloride, $AuCl_3$, from which the metal may be obtained.

Chlorine is used for the preparation of many substances such as carbon tetrachloride, CCl_4, and chloroform, $CHCl_3$,

because of its ability to replace hydrogen in organic molecules. Some of the organic chlorine compounds are very toxic and have been used or proposed as war gases. Chlorine is thus used for the discomfort and death of man as well as for the preservation of his comfort and health.

HYDROCHLORIC ACID

7. Introduction. We have seen that hydrogen and chlorine combine to form a gas, *hydrogen chloride*, HCl. When this gas is dissolved in water we have hydrochloric acid. This acid was known to the early experimenters, and Priestley named it "marine-acid gas" since it was prepared from sea-salt. It was later named *muriatic acid* and is known by that name today by plumbers, who use it in soldering. Davy showed it to be composed of hydrogen and chlorine, and you will remember that it was the first acid known that did not contain oxygen. It belongs to a group of acids known as the hydracids, which consist only of hydrogen and a non-metallic element.

8. Preparation of hydrochloric acid.

A. Laboratory method.

By the action of sulphuric acid upon sodium chloride. Hydrochloric acid may be prepared by heating a mixture of sodium chloride and sulphuric acid, and dissolving the resulting gas in water. This is the general method of obtaining a stable volatile acid from one of its salts. The apparatus is similar to that used for the preparation of sulphur dioxide and the gas is collected by the upward displacement of air. The gas may be led directly into water to produce the acid. A pneumatic trough cannot be used because of the solubility of the gas in water. In this reaction the acid salt, sodium bisulphate, may be produced.

$$\mathbf{NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl}$$

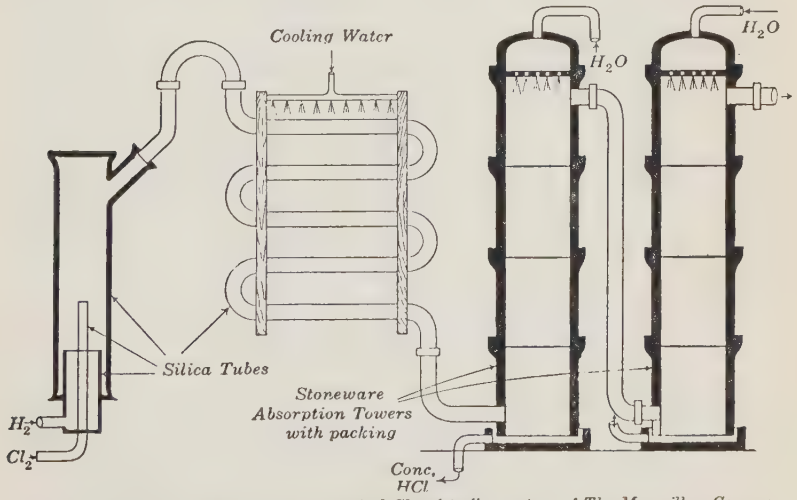
B. Industrial methods.

(1) *By the heating of sodium chloride with sulphuric acid.* The laboratory method of preparing hydrochloric acid may be employed on an industrial scale. In this case the larger quantities of sodium chloride used and the greater heat employed lead to the production of the normal instead of the acid salt.

$$2\ NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ HCl$$

There is a more economical use of the sulphuric acid in the industrial than in the laboratory method, since twice as much hydrogen chloride is produced for the same quantity of sulphuric acid. The crude sodium sulphate produced by this process is known as *salt cake.*

(2) *By the direct union of hydrogen and chlorine.* Hydrochloric acid may be prepared industrially by burning hydrogen in an atmosphere of chlorine. The hydrogen and chlorine may be obtained from the electrolysis of a solution of sodium chloride (see Fig. 142). The hydrogen chloride produced by this process is dissolved in water to obtain the acid.



From Black & Conant: "New Practical Chemistry", courtesy of The Macmillan Company

Fig. 142. Apparatus for the commercial synthesis of hydrochloric acid.

9. Physical properties of the gas and the acid. Hydrogen chloride is a colourless gas with a sharp irritating odour. Its molecular weight of 36.47 indicates the molecular formula HCl. One volume of water will dissolve about 500 volumes of the gas at 0°C. and 1 atmosphere pressure. A saturated solution of the gas in water contains about 39 per cent of the gas; the ordinary concentrated acid contains about 37 per cent. If the solution is boiled not all of the gas will be given off, but a constant-boiling solution will be obtained which boils at 110°C. at 1 atmosphere and contains about 20 per cent by weight of hydrogen chloride. The composition of this constant-boiling solution varies with the pressure, showing that the solution in water is not a compound. The extreme solubility of this gas in water can be demonstrated by the ammonia fountain, a piece of apparatus used frequently to show the great solubility of a gas in water (see Fig. 89B).

10. Chemical properties of the gas and the acid. Hydrogen chloride is a very stable gas and the anhydrous gas and liquid are very inactive. The dry gas does not attack metals at low temperatures and does so very slowly at high temperatures. The acid made by dissolving the gas in water behaves like any *strong* acid (see Chap. 23). It has a sour taste, turns blue litmus red and contains replaceable hydrogen. All metals above hydrogen in the electro-chemical series react with the acid to produce hydrogen and a chloride of the metal.

$$Ca + 2\,HCl \longrightarrow CaCl_2 + H_2$$
$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$$

Hydrogen chloride reacts with ammonia to produce a dense white smoke of ammonium chloride by the direct addition of the two compounds.

$$HCl + NH_3 \longrightarrow NH_4Cl$$

This reaction is used as a test for the *gas*. A rod moistened with concentrated ammonium hydroxide is placed in the gas to be tested. If the gas is hydrogen chloride the white fumes will be seen immediately. Conversely, a solution of hydrogen chloride is used to find leaks in ammonia pipes in a refrigerating plant. This same reaction accounts for the white deposit found on laboratory windows and on glassware, because of the large quantities of these reagents used in most laboratories.

The test for the chloride ion, produced by the hydrochloric acid and present in solutions of soluble chlorides, is to add a solution of silver nitrate. Double decomposition occurs and silver chloride, which is quite insoluble, is precipitated.

$$AgNO_3 + HCl \longrightarrow \underline{AgCl} + HNO_3$$

$$BaCl_2 + 2\ AgNO_3 \longrightarrow 2\ \underline{AgCl} + Ba(NO_3)_2$$

In the use of this reaction to determine the presence of chlorides it is to be noted that the precipitation of the silver chloride takes place in the presence of nitric acid. Some silver salts beside silver chloride are insoluble in water, but these salts are soluble in nitric acid. To be sure that the precipitate is silver chloride a few drops of nitric acid are added before adding the silver nitrate.

11. The uses of hydrochloric acid. Hydrochloric acid is one of the most widely used acids in industry because of its ability to dissolve the oxides of the metals. It is more expensive than sulphuric acid and for some reactions it is not as satisfactory since it is more volatile and will act as a reducing agent. It is used because almost all chlorides are soluble in water. It is a commonly used laboratory reagent, appearing as dilute and concentrated solutions on the shelves, and is used frequently in chemical analysis.

Hydrochloric acid is used to "pickle" iron in the preparation of galvanized sheet metal. In this process clean sheet

iron is dipped in molten zinc so the sheets are first dipped in a bath of hydrochloric acid to remove traces of oxide from the surface of the iron. The acid is also used in the manufacture of drugs, dyes, glue and textiles, and in the preparation of the chlorides of metals.

Small amounts of hydrochloric acid are present in the gastric juice secreted in the stomach and produced from sodium chloride consumed in the diet.

Question Summary

1. Give an account of the discovery of chlorine.

2. How does chlorine occur in the earth?

3. (*a*) Describe the laboratory method of preparing chlorine by manganese dioxide and hydrochloric acid.
(*b*) Describe the laboratory method of preparing chlorine by potassium permanganate and hydrochloric acid.
(*c*) Describe the laboratory method of preparing chlorine by manganese dioxide, sodium chloride and sulphuric acid.
(*d*) Describe the industrial method of preparing chlorine.

4. What are the physical properties of chlorine?

5. (*a*) Describe the action of chlorine on metals.
(*b*) Describe the action between chlorine and hydrogen.
(*c*) Describe the action between chlorine and water.

6. (*a*) Describe the action of chlorine as a bleaching agent.
(*b*) Describe the action of chlorine as a disinfectant.
(*c*) Name some other uses for chlorine.

7. What is meant by "muriatic acid" and by whom is it used?

8. (*a*) Describe the laboratory preparation of hydrogen chloride.
(*b*) Describe the industrial preparation of hydrogen chloride.

9. Give the physical properties of hydrogen chloride and hydrochloric acid.

10. (*a*) Give the chemical properties of hydrochloric acid.
(*b*) What is a test for hydrogen chloride?
(*c*) What is a test for hydrochloric acid?

11. Give the uses of hydrochloric acid.

Chapter **28**

Fluorine, Bromine, Iodine

FLUORINE

1. Occurrence. Fluorine is not found in the free state because of its great activity. It is found in nature in the minerals, *fluorspar*, CaF_2, and *cryolite*, $AlF_3.3NaF$. Fluorine is found in small quantities in the bones of animals, especially in the teeth. It has been suggested that variations in the prevalence of tooth decay may be due to the amount of fluorine in drinking water.

2. Preparation of fluorine. It is impossible to oxidize hydrofluoric acid with manganese dioxide and obtain free fluorine, as was done with hydrochloric acid in the preparation of chlorine. It was recognized that this failure was due to the great chemical activity of fluorine, which makes it more difficult to separate from its compounds than chlorine, bromine or iodine. For many years all attempts to obtain the free element were unsuccessful and were accompanied by some fatal accidents. In 1886 it was obtained by Moissan by the electrolysis of a solution of potassium fluoride in pure anhydrous hydrofluoric acid. Moissan used a cell made from an alloy of platinum and iridium, using electrodes made from the same alloy and set in stoppers of fluorspar. This cell is shown in Fig. 143. The cell was cooled to about $-23°C.$ at which temperature the hydrofluoric acid is a liquid. Fluorine was liberated at the anode and hydrogen at the cathode. Fluorine is now prepared in a cell constructed of magnesium, monel metal, or copper, by the electrolysis

of molten potassium acid fluoride, KHF_2, using graphite electrodes which are not attacked readily by the gas. The cell becomes protected from excessive action by the formation of a protective coating of a fluoride.

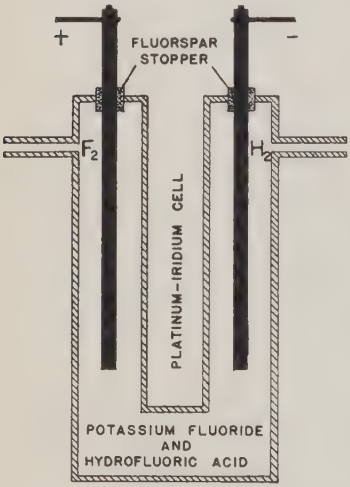
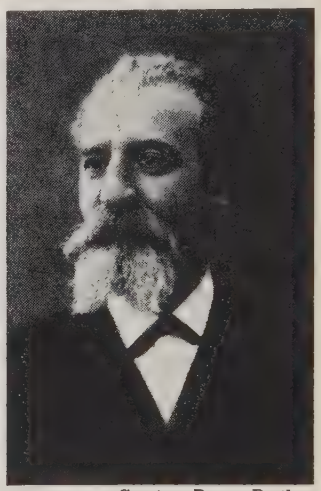


Fig. 143.



Courtesy Brown Brothers

Fig. 144.

Fig. 143. Diagram of electrolysis cell for fluorine.

Fig. 144. Henri Moissan (1852-1907), French professor of chemistry, was the first one to isolate fluorine.

3. Properties of fluorine. Fluorine is a pale greenish-yellow gas with a lighter colour than chlorine. Its molecular formula is F_2 and its density is slightly greater than that of air. It is not soluble in water. Fluorine is very dangerous to handle and it is fatal to breathe it.

Fluorine unites with every element except chlorine, nitrogen and the inert gases. Elements which unite with chlorine react with fluorine with greater vigour. It explodes when mixed with hydrogen at ordinary temperatures, even in the dark. It reacts vigorously with water, forming hydrofluoric acid and oxygen,

$$2\ H_2O + 2\ F_2 \longrightarrow 4\ HF + O_2$$

at the same time producing some fluorine oxide, F_2O. Fluorine displaces chlorine, bromine and iodine from their compounds. You will recall that chlorine replaces bromine and iodine. Fluorine is more active than chlorine and it displaces not only these elements but all non-metallic elements from their compounds.

4. Hydrogen fluoride and hydrofluoric acid. Hydrogen fluoride may be prepared by heating a mixture of calcium fluoride and concentrated sulphuric acid in a lead or platinum retort since it is very stable to heat and to oxidizing agents. The gas is led into water in which it is very soluble and hydrofluoric acid is formed.

$$\mathbf{CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2F_2}$$

Hydrogen fluoride is a colourless gas which is very soluble in water and fumes in moist air. The vapour density indicates the formula H_2F_2 below 40°C., although it may dissociate into HF at higher temperatures. The existence of acid salts, such as $NaHF_2$ and KHF_2, appears to confirm the formula H_2F_2.

Hydrofluoric acid acts upon silica (sand) and silicates to form the gas silicon tetrafluoride, SiF_4. Glass is a mixture of sodium and calcium silicates and is therefore attacked by the acid. This is the principle of the etching of glass.

$$\mathbf{Na_2SiO_3 + 3\ H_2F_2 \longrightarrow SiF_4 + 2\ NaF + 3\ H_2O}$$
$$\mathbf{CaSiO_3 + 3\ H_2F_2 \longrightarrow SiF_4 + CaF_2 + 3\ H_2O}$$

The glass is covered with paraffin wax and from the portions to be etched the wax is cut away with a sharp instrument. On exposure to the vapour of H_2F_2 the uncovered parts of the glass become roughened. Burettes and graduated glassware are etched in this manner. An aqueous solution of hydrofluoric acid may be employed, in which case a smooth depression is obtained.

5. Uses of fluorine compounds. There is no use for fluorine itself, perhaps because its great activity makes it difficult to prepare and handle, but its compounds have many uses. Since our teeth contain a mineral called apatite, $3Ca_3(PO_4)_2.CaF_2$, a small amount of fluorides in drinking water is thought to aid in preventing decay of the teeth. Fluospar, CaF_2, is used as a flux which forms fusible compounds with substances that do not melt easily. Cryolite is used as a flux in the preparation of aluminum. Sodium fluoride is used as an insecticide, a flux, and for the treatment of wood to prevent attack by fungi. Hydrofluoric acid is used as a laboratory reagent in the determination of silica, SiO_2 and for that purpose is available in wax or plastic bottles. Both the acid and a mixture of calcium fluoride and sulphuric acid are used for etching glass. Organic compounds of fluorine are of interest as some of them are toxic and could be used as war gases.

BROMINE

6. Occurrence. Bromine was prepared by Liebig and other experimenters, but they believed that it was a compound of chlorine and iodine. In 1826 Balard prepared the element from the liquid remaining when sodium chloride is crystallized from brine and named it *bromine* from the Greek word meaning "stench". Bromine does not occur in the free state because of its great activity, but it occurs usually as the bromides of sodium, potassium and magnesium in sea-water, sea-salt deposits, and in the waters of the Dead Sea and the Great Salt Lake.

7. Preparation of bromine.

A. Laboratory Method.

Bromine may be prepared in the laboratory by heating a mixture of sodium bromide, manganese dioxide and concentrated sulphuric acid. Hydrobromic acid is produced,

oxidized by the manganese dioxide, and bromine is set free.

$$2\ NaBr + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ HBr$$
$$4\ HBr + MnO_2 \longrightarrow MnBr_2 + 2\ H_2O + Br_2$$

This may be expressed in one equation as follows:

$$4\ NaBr + MnO_2 + 2\ H_2SO_4 \longrightarrow 2\ Na_2SO_4 + MnBr_2 + 2\ H_2O + Br_2$$

The reaction is carried out in a glass retort since bromine attacks rubber stoppers and tubing. The apparatus is shown in Fig. 145. Since the bromine is liquid at room temperature it may be collected in a flask immersed in cold water.

B. Industrial Method.

Bromine may be obtained from sea-water by the action of chlorine. Since the process is more effective at higher temperatures the sea-water is run into basins where it is warmed by the sun before being used. The water is then sprayed into towers through which chlorine is passing. The bromine is displaced from its compounds by the action of the chlorine and is removed from the water by passing air through it. The bromine-laden air is passed to another tower where it reacts with a solution of sodium carbonate to produce sodium bromide and sodium bromate.

$$3\ Br_2 + 3\ Na_2CO_3 \longrightarrow 5\ NaBr + NaBrO_3 + 3\ CO_2$$

This mixture of salts is then treated with sulphuric acid to liberate the bromine.

$$5\ NaBr + NaBrO_3 + 3\ H_2SO_4 \longrightarrow 3\ Na_2SO_4 + 3\ H_2O + 3\ Br_2$$

Much bromine is needed to make the ethyl bromide for anti-knock gasolines.

8. Physical properties of bromine. At room temperature bromine is a dark red liquid with a boiling point of

59°C. and a freezing point of −7.3°C. Its specific gravity at 0°C. is 3.1. It is not very soluble in water, but is more so than chlorine. The aqueous solution is known as *bromine water*. Bromine has a greater solubility in certain organic liquids than in water, dissolving easily in carbon tetrachloride, carbon disulphide, chloroform and ether. It has a disagreeable odour and is very irritating to the eyes, nose and throat. If the liquid is spilled on the skin it causes painful burns which are slow in healing. It must be handled with great caution at all times.

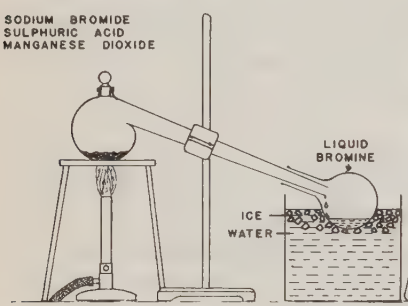


Fig. 145. Preparation of bromine.

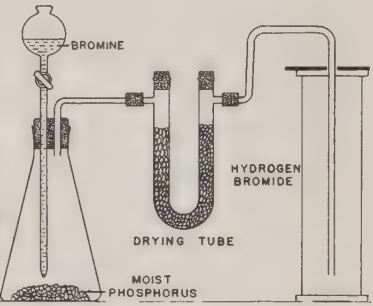


Fig. 146. Preparation of hydrogen bromide.

9. Chemical properties of bromine. Bromine resembles chlorine in its chemical behaviour but it is less active. It reacts with the more active metals but does not combine with the less active ones. It does not combine directly with carbon, oxygen, nitrogen or chlorine; but it forms a tri-bromide, PBr_3, and a penta-bromide, PBr_5, with phosphorus, and a mono-bromide, S_2Br_2, with sulphur. Bromine reacts slowly with hydrogen at low temperatures but more actively at high temperatures and in bright light. It reacts less actively than chlorine with the hydrocarbons. When dissolved in water it reacts in a similar manner to chlorine but more slowly. Hydrobromous acid, HBrO, is formed and this breaks up into hydrobromic acid and oxygen. A jet of burning hydrogen will continue to burn in bromine vapour,

producing hydrogen bromide, which fumes in moist air like hydrogen chloride. When they are finely divided some of the more active metals like zinc will combine directly with bromine when thrown into the vapour.

10. Hydrogen bromide and hydrobromic acid. Hydrobromic acid is prepared easily in the laboratory by allowing bromine to drop upon red phosphorus that has been moistened with water. The apparatus is shown in Fig. 146. The U-tube contains glass beads mixed with dry red phosphorus to absorb any bromine that may be carried over with the stream of gas. The hydrogen bromide may be collected by the upward displacement of air as shown, or it may be dissolved immediately in water to form hydrobromic acid. When the bromine drops on the red phosphorus it forms phosphorus tri-bromide.

$$2\ P + 3\ Br_2 \longrightarrow 2\ PBr_3$$

The phosphorus tri-bromide is acted upon immediately by the water, and hydrogen bromide and phosphorous acid are produced.

$$PBr_3 + 3\ H_2O \longrightarrow 3\ HBr + H_3PO_3$$

The phosphorous acid is dissolved in the water and remains in the flask, while the hydrogen bromide is liberated. This reaction of water with phosphorus tri-bromide is a double decomposition in which water takes part and is known as *hydrolysis*. The phosphorus tri-bromide is said to be hydrolyzed.

It might be supposed that hydrogen bromide could be prepared by the action of sulphuric acid upon a bromide as

$$H_2SO_4 + NaBr \longrightarrow NaHSO_4 + HBr$$

The action takes place momentarily but the nascent hydrogen bromide is oxidized rapidly by the sulphuric acid. If the reaction is attempted some hydrogen bromide will be

produced but it will be mixed with bromine and sulphur dioxide which are the products of the oxidation by the sulphuric acid.

$$H_2SO_4 + 2\ HBr \longrightarrow SO_2 + 2\ H_2O + Br_2$$

This action is, however, used as a test for a bromide, when the production of the red bromine vapour may be noted.

Hydrogen bromide is a colourless gas with an irritating odour similar to that of hydrogen chloride. It is quite stable and forms a strong acid with water. Chlorine water added to a solution of a bromide displaces the bromine. If a few drops of carbon disulphide are shaken with the liquid the bromine will dissolve in the carbon disulphide which will settle to the bottom. The bromine dissolves more readily in the carbon disulphide than in the water and may be recognized easily by its reddish-brown colour in the solution. Hydrobromic acid is not used much in the laboratory since its reactions are not very different from those of hydrochloric acid and the latter is more easy to prepare. With a solution of a bromide silver nitrate produces a yellowish precipitate of silver bromide.

$$AgNO_3 + HBr \longrightarrow \underline{AgBr} + HNO_3$$

11. Uses of bromine and its compounds. Bromine is very useful for replacing hydrogen in organic molecules and is used chiefly in the preparation of ethylene bromide. This figures in the manufacture of anti-knock substances for gasoline. The bromides react with silver nitrate to give silver bromide which is used in the preparation of emulsion for photographic films and papers because it is more sensitive to decomposition by light than silver chloride. Sodium and potassium bromides are used in medicine as sedatives, and bromine itself in the manufacture of several organic compounds, among which are dyes and tear gas.

IODINE

12. Occurrence. Shortly after Davy had found that "marine acid oxide" was the element chlorine, Courtois prepared iodine by heating the ashes of certain sea-weeds with concentrated acid, but he did not recognize it as an element. In 1814 Gay-Lussac concluded that the substance prepared by Courtois was an element and named it *iodine* from the Greek meaning "violet".

Iodine is not found in the free state but it occurs as iodides in sea-water and brines. It is also found in the ashes of certain sea-weeds. A small amount of iodine is necessary for the proper health of the human body. If there is a deficiency of iodine the thyroid gland in the neck will not function properly and will become swollen. This swelling of the neck is known as *goitre*. Normally there is sufficient iodine furnished by foods such as green beans, spinach, butter and milk but sometimes sodium iodide is added to salt which is to be used for seasoning. Salt treated in this way is said to be *iodized*. If the diet includes sea foods there is generally sufficient iodine provided so that people who eat that type of food are not as liable to goitre as those who do not. Goitre is practically unknown among people living near the sea-coast. Most of the world's supply of iodine comes from the sodium nitrate deposits in Chile where it is found as sodium iodate, $NaIO_3$.

13. Preparation of iodine.

A. Laboratory Method.

Iodine may be prepared from sodium or potassium iodide by a method similar to that used for the preparation of bromine. Sodium iodide, manganese dioxide and concentrated sulphuric acid are placed in a beaker over which is placed an evaporating dish containing cold water. This apparatus is arranged as shown in Fig. 147. When the

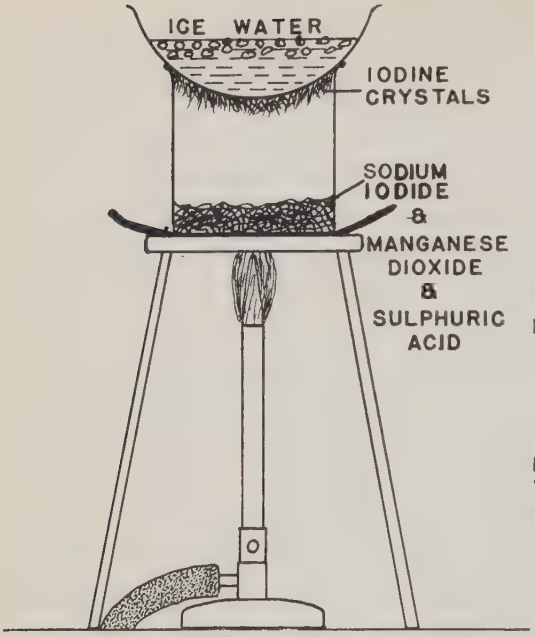


Fig. 147.

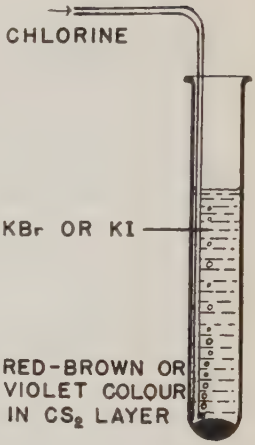


Fig. 148.

Fig. 147. Preparation and sublimation of iodine.

Fig. 148. Bromides or iodides may be detected by adding chlorine and shaking with carbon disulphide. Chlorine displaces bromine to give a red-brown colour and displaces iodine to give a violet colour.

mixture in the beaker is heated gently iodine is liberated.

$$3\ H_2SO_4 + MnO_2 + 2\ NaI \longrightarrow MnSO_4 + 2\ NaHSO_4 + 2\ H_2O + I_2$$

The iodine vapour will condense to violet-black crystals on the bottom of the cold dish. When iodine vapour condenses it does not form a liquid but goes directly to the solid state. The reverse process, where a solid changes to a gas without passing through the liquid state, is known as *sublimation*. The iodine may be purified by sublimation of the crystals in an inert atmosphere.

B. Industrial Method.

Iodine is obtained from the sodium iodate, found in the

Chile deposits, by the reducing action of sodium bisulphite.

$$2\ NaIO_3 + 5\ NaHSO_3 \longrightarrow 2\ Na_2SO_4 + 3\ NaHSO_4 + H_2O + I_2$$

The iodine is recovered from the other substances produced in the reaction by evaporating to dryness and heating the residue. The iodine will sublime and may be condensed to the solid crystals.

14. Properties of iodine. At room temperature iodine is in the form of violet-black crystalline plates. Under pressure of 90 mm. of Hg. its melting point is 114°C. Iodine dissolves slightly in water, but dissolves more readily in organic liquids such as chloroform, ether, carbon tetrachloride and carbon disulphide. It also dissolves readily in a solution of an iodide. The iodine usually found in household medicine chests is a 5 per cent solution in ethyl alcohol. Solutions in alcohol are known as *tinctures*.

Iodine is less active chemically than fluorine, chlorine and bromine but its behaviour is similar. It combines with them and with oxygen, and it reacts with phosphorus to form the triiodide, but not a pentiodide. It reacts with most of the metals. At low temperatures it reacts slowly with hydrogen, but it forms hydrogen iodide at higher temperatures, in a bright light, and under the action of a catalyst.

15. The preparation of hydrogen iodide and hydriodic acid. Hydrogen iodide may be prepared by a method similar to that used for the preparation of hydrogen bromide. Red phosphorus is mixed with iodine and water allowed to drop upon the mixture. The phosphorus triiodide which is formed is hydrolyzed forming phosphorous acid and hydrogen iodide.

$$2\ P + 3\ I_2 \longrightarrow 2\ PI_3$$
$$2\ PI_3 + 6\ H_2O \longrightarrow 6\ HI + 2\ H_3PO_3$$

The action of sulphuric acid on an iodide does not give pure hydrogen iodide. Hydrogen iodide is less stable than hydro-

gen bromide and reduces the sulphuric acid to hydrogen sulphide.

$$H_2SO_4 + 8\ HI \longrightarrow H_2S + 4\ H_2O + 4\ I_2$$

This reaction is used as a test for an iodide, as the free iodine can be recognized by its violet-coloured vapour when the substances are heated in a tube. The hydrogen sulphide may also be detected by its odour. You will note that the sulphuric acid is reduced to hydrogen sulphide by HI but only to sulphurous acid by HBr.

Hydrogen iodide is a colourless gas with an irritating odour. It is very soluble in water, forming hydriodic acid. The gas is the least stable of the compounds of hydrogen with these four substances and will decompose into its constituents when heated to 180°C. Since it loses its hydrogen so readily it may be burned in oxygen, producing free iodine.

$$4\ HI + O_2 \longrightarrow 2\ H_2O + 2\ I_2$$

It combines violently with chlorine forming hydrogen chloride.

$$2\ HI + Cl_2 \longrightarrow 2\ HCl + I_2$$

Hydriodic acid reacts like hydrochloric and hydrobromic acids. It loses its hydrogen so easily that it will react with atmospheric oxygen and a solution of the acid will turn brown from the presence of free iodine when exposed to the air. Because of this ease with which it parts with its hydrogen, hydriodic acid is used frequently as a reducing agent. Chlorine water or bromine water added to a solution of hydriodic acid or an iodide will displace iodine (see Fig. 148).

$$Cl_2 + 2\ NaI \longrightarrow 2\ NaCl + I_2$$

The free iodine may be recognized by adding a few drops of carbon disulphide and shaking the mixture. The iodine

dissolves in the carbon disulphide which settles to the bottom of the tube to produce a violet solution. The common test for free iodine is the addition of starch solution, which acquires a deep blue colour in the presence of free iodine.

The tests just mentioned apply only to *free* iodine. The iodide *ion* may be detected by the addition of silver nitrate to the solution of an iodide, when the yellow silver iodide will be precipitated.

$$AgNO_3 + KI \longrightarrow \underline{AgI} + KNO_3$$

16. Uses of iodine and its compounds. Iodine is used frequently as an antiseptic, usually in the form of the tincture. Iodoform, CHI_3, is often similarly used. Because iodine replaces hydrogen readily it is used in the manufacture of many organic chemicals, such as the aniline dyes. Together with hydrogen iodide it is used to prepare the iodides of the metals, of which sodium and potassium iodides are the most important. Silver iodide is used in the preparation of photographic emulsions because it is very sensitive to decomposition by light. The use of iodine in the treatment of goitre has been mentioned. Thyroxin, $C_{15}H_{11}O_4NI_4$, which may be extracted from the thyroid glands of animals or prepared synthetically is used in the treatment of diseased thyroid glands.

17. The halogen family. The elements fluorine, chlorine, bromine and iodine are called the halogens or "formers of sea salt". Their properties show a gradual change from element to element starting with fluorine and ending with iodine. For this reason they are referred to as the halogen family. The gradation of properties will be revealed more clearly if we summarize them in tabular form. Both their physical and their chemical properties show a progressive change from element to element as the atomic weight increases. A few of these are shown in Table 22.

TABLE 22 —COMPARISON OF PROPERTIES OF HALOGENS

Physical properties	*Fluorine*	*Chlorine*	*Bromine*	*Iodine*
Atomic weight.....	19.00	35.457	79.916	126.92
Melting point, °C...	—223	—101.6	—7.3	114
Boiling point, °C....	—187	—34.5	59.0	184
Density.....	1.14	1.51	3.18	4.9
Colour.....	Pale green	Greenish-yellow	Red-brown	Violet
State.....	Gas	Gas	Liquid	Solid
Chemical activity				
With metals.....	All burn	Many burn	Few burn	All corrode but Pt.
With non-metals....	All react except O, Cl, N.	All react but O, F, Br, C, N.	None react but S, Se, Te, P, As.	None react but P and S
With hydrogen.....	Explosive	Explosive in sunlight	Requires heat	Very slow
With water.....	Rapidly forms H_2F_2 & O_2	Slowly forms HCl & O_2	No reaction	No reaction
Hydride stability....	Extremely stable	Stable	Unstable	Very unstable
Oxidizing power....	Strongest	Strong	Moderate	Weak
Binary compound valence.....	−1	−1	−1	−1

We can say that although all the halogens are alike in that they are non-metals, have an irritating odour, are poisonous, coloured, very active, and univalent in their binary compounds, they show a gradation of intensity in these properties with atomic weight. In this way we can form a general opinion about their compounds. For example, NaF, NaCl, NaBr, NaI, will be somewhat alike in crystal form, solubility in water, degree of ionization and other properties. The

ability to generalize about a group of elements greatly simplifies the task of understanding their behaviour.

Question Summary

1. How does fluorine occur on the earth?

2. (*a*) Why cannot fluorine be prepared in the same manner as chlorine?
   (*b*) Describe the preparation of fluorine.

3. What are the physical and chemical properties of fluorine?

4. (*a*) How is hydrogen fluoride prepared?
   (*b*) Explain the etching of glass.

5. Give some of the uses of fluorine compounds.

6. How does bromine occur on the earth?

7. (*a*) Describe the laboratory method of preparing bromine.
   (*b*) Describe the industrial method of preparing bromine.

8. What are the physical properties of bromine?

9. What are the chemical properties of bromine?

10. (*a*) How is hydrogen bromide prepared?
    (*b*) What are the properties of hydrobromic acid?

11. Give some of the uses of bromine and its compounds.

12. (*a*) How does iodine occur in nature?
    (*b*) How is iodine utilized by the human body?

13. (*a*) Describe the laboratory preparation of iodine.
    (*b*) Describe the industrial preparation of iodine.

14. Give the properties of iodine.

15. (*a*) How is hydrogen iodide prepared?
    (*b*) What are the properties of hydriodic acid?

16. Give some of the uses for iodine and its compounds.

17. (*a*) How do some of the physical properties of the halogens vary with the atomic weight of the elements?
    (*b*) How do some of the chemical properties vary and yet remain very similar?

Chapter **29**

The Alkali Metals

1. Introduction. We have just finished the study of a family of non-metallic elements. We shall now consider another family, this one consisting of five metals, *sodium*, *potassium*, *lithium*, *rubidium* and *cesium*. These elements have sufficiently similar properties for them to be considered as a family, known as the *alkali metals*. The substances which we now know as sodium and potassium hydroxides were known as "fixed alkalis"; it was believed that they were the oxides of undiscovered elements. Because of their relations to these two alkalis, these metals, when they were discovered, were named the "alkali metals" and the name has been given to the whole family. While the halogens all showed a negative valence of 1 the alkali metals show a *positive* valence of 1. All these metals are white, with a brilliant lustre, and are so soft that they can be cut with a knife. They unite with oxygen so readily that they must be stored under the surface of an oil. On first examination one would not think that they were metals at all, since we are accustomed to think of metals as hard and durable substances; but if we examine the chemical behaviour of these elements we find that they are typically metallic. Their oxides are the anhydrides of strong bases and their familiar compounds are those in which the metal acts as a positively charged ion. This is directly opposite from the behaviour of the halogens, which provide negative ions and whose oxides are the anhydrides of acids. Of the five alkali metals, sodium and potassium are the most familiar and they will be considered in greater detail.

SODIUM

2. Occurrence. The most common compound containing sodium is sodium chloride but it is also found in certain silicate rocks, and in other salts. Sodium nitrate is found in Chile, sodium carbonate occurs in Egypt, sodium sulphate is abundant in Canada and borax is found in the United States.

3. Preparation of metallic sodium. Sodium is prepared by the electrolysis of the fused hydroxide as it was done originally by Davy. This is done in the cell devised by Castner, shown in Fig. 150.

Courtesy Fisher Scientific Co.

Fig. 149.

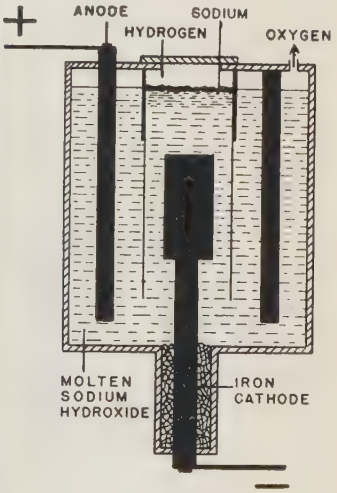


Fig. 150.

Fig. 149. Sir Humphrey Davy (1778-1829), an English chemist, was the first to prepare sodium and potassium by electrolysis.

Fig. 150. The Castner process.

The outside vessel is made of iron and contains the sodium hydroxide. This is kept in a molten state by the resistance encountered by the electricity in passing through the cell, but an additional source of heat is provided by gas burners. The cathode consists of an iron rod rising through the vessel and being supported by some of the solid sodium hydroxide at

the bottom. The anode consists of an iron ring which surrounds the cathode. A gauze cylinder with a solid iron top is placed over the cathode to prevent the products of electrolysis from becoming mixed. Sodium and hydrogen are liberated at the cathode. The sodium floats to the top of the molten sodium hydroxide inside of the iron gauze cylinder and is protected from the action of the air by the presence of the hydrogen. The oxygen which is liberated at the anode is allowed to escape from the cell through a vent.

Since sodium hydroxide is prepared from sodium chloride, it eliminates a step in the process if the latter substance can be used in the production of sodium. Large quantities of sodium are prepared by the electrolysis of molten sodium chloride in the Downs cell shown in Fig. 151.

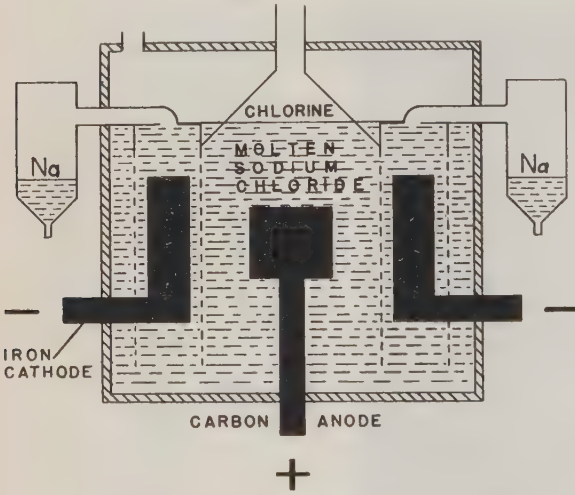


Fig. 151. The Downs cell for the production of sodium metal by the electrolysis of fused sodium chloride.

The cathode is an iron ring which is separated from the central iron anode by a diaphragm. The sodium rises to the top of the liquid in the cathode compartment and flows off into a vessel where it is collected under the surface of an oil. The chlorine liberated at the anode is allowed to escape from the cell. One disadvantage in the use of sodium chloride as an electrolyte for preparing sodium is that it requires a temperature above bright red heat to become a liquid.

4. Properties of sodium. Sodium is a very active metal, combining readily with most of the non-metals. It forms two oxides, Na_2O and Na_2O_2, and unites with sulphur and the halogens. It displaces hydrogen from most of the acids,

forming the sodium salt of the acid. You have seen how it reacts vigorously with water to liberate gaseous hydrogen and leave sodium hydroxide. It is an active reducing agent and will reduce many of the metals from their ores. It forms alloys with some of the metals, that with mercury, *sodium amalgam*, being the most important. The alloy of sodium and potassium is liquid at room temperature. Sodium and some of its compounds impart a characteristic yellow colour to a flame. This is used in chemical analysis to detect the presence of sodium. The flame is examined in an instrument known as a *spectroscope* which separates light into its component wave lengths.

5. Uses of sodium. Most of the compounds of sodium are prepared from the chloride but there are a few, such as sodium peroxide and sodium cyanide, which are prepared from metallic sodium. Sodium is used in the preparation of lead tetraethyl, which is used in ethyl gasoline, and certain organic compounds. In laboratory practice it is frequently employed to remove water from organic liquids. It has a limited use as a reducing agent in obtaining metals from their ores. Sodium vapour is utilized in electric lamps which give a light that is very distinct through fog. These lights are useful for illumination at air-ports and on highways.

6. The oxides of sodium. Sodium forms two oxides, *sodium oxide*, Na_2O, and *sodium peroxide*, Na_2O_2. Sodium oxide may be made by heating the hydroxide with sodium.

$$2\ NaOH + 2\ Na \longrightarrow 2\ Na_2O + H_2$$

When sodium burns in oxygen, the peroxide is formed.

$$2\ Na + O_2 \longrightarrow Na_2O_2$$

Sodium peroxide is a strong oxidizing agent. It reacts with acids and with water to form hydrogen peroxide.

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$
$$Na_2O_2 + 2\ H_2O \longrightarrow 2\ NaOH + H_2O_2$$

Unless the temperature is kept low the heat of the latter reaction decomposes the hydrogen peroxide into water and oxygen. At room temperatures the dropping of water on sodium peroxide is a means of preparing oxygen (see Chap. 5. sec. 3).

7. Sodium hydroxide, NaOH, commonly known as *caustic soda*, is a familiar laboratory reagent. It is prepared industrially by two methods: the action of calcium hydroxide on sodium carbonate, and the electrolysis of sodium chloride solutions. In the first method, sodium carbonate is added to a suspension of calcium hydroxide in water, when the following reaction occurs:

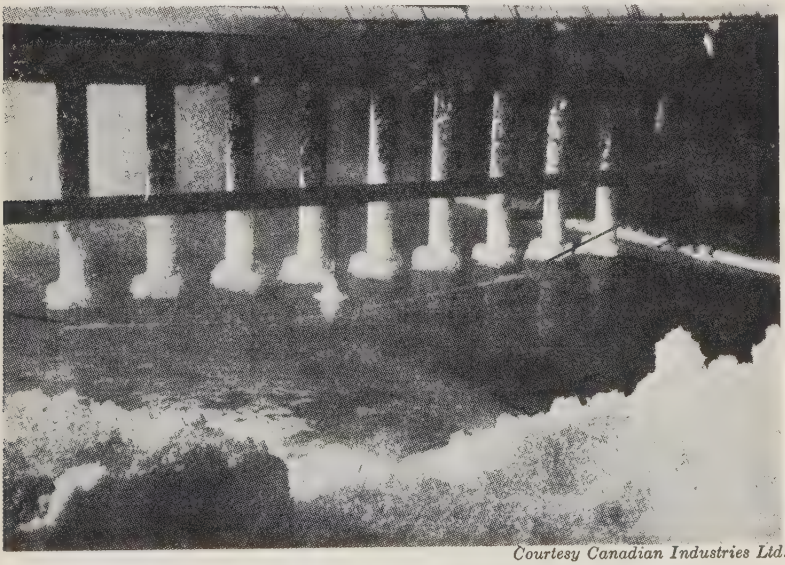
$$\mathbf{Ca(OH)_2 + Na_2CO_3 \longrightarrow \underline{CaCO_3} + 2\ NaOH}$$

The insoluble calcium carbonate is filtered off and the solution of sodium hydroxide is evaporated to dryness and then fused. The molten hydroxide may be cast into sticks or pellets or broken up into flakes. Sodium hydroxide is produced during the electrolysis of sodium chloride solutions in the preparation of chlorine (see Chap. 27, sec. 3). Sodium hydroxide prepared by this method contains sodium chloride which will separate if the solution is concentrated. It is impossible to remove all traces of chloride by concentration, and if a specially pure product is desired the sodium hydroxide may be dissolved in alcohol in which the impurities are insoluble. The alcoholic solution is then filtered and the hydroxide recovered by evaporation of the solvent.

Sodium hydroxide is deliquescent and is very soluble in water. Its solutions will absorb carbon dioxide from the air and form sodium carbonate, which is the most common impurity present when aqueous solutions of sodium hydroxide are used. When pure solutions are desired they must be protected from the air to prevent the absorption of carbon dioxide. Sodium hydroxide reacts with the silicates in glass

and a bottle in which a solution is kept will become etched. Solutions of the hydroxide should not be kept in glass-stoppered bottles because the etching will cause the stoppers to stick. Solutions of sodium hydroxide feel soapy when rubbed between the fingers and they possess all the characteristics of a strong base. They form soluble compounds with animal fats and so they are useful for cleaning.

8. Sodium chloride, NaCl, is the familiar and important substance known as *common salt.* It is found in sea-water, salt lakes, and in deposits which have been produced by the evaporation of inland seas many thousands of years ago. The average amount of sodium chloride in sea-water is 3 per cent but in the Dead Sea and the Great Salt Lake it rises to 20 per cent. Important salt deposits are found in Stassfurt in Germany, in many parts of the United States and in Canada. The currently operated Canadian deposits are found near Windsor, Ontario; Unity, Saskatchewan; and



Courtesy Canadian Industries Ltd.

Fig. 152. The discharge end of a salt grainer showing crystallized salt in the foreground.

at Malagash and Amherst in Nova Scotia. In some cases the salt is obtained from deposits by flooding and pumping the resulting brine to the surface. From other deposits the salt is obtained by ordinary mining. Pure salt is obtained by evaporation of solutions of the crude salt (see Fig. 152).

The coarse salt used for fish-curing is obtained from either mines, brines, or from the sea-water. It is produced from sea-water in the West Indies, California, and the Mediterranean, where the water is evaporated in large ponds by the sun and the salt crystals raked off the bottom of the ponds. Table salt is usually crystallized from solutions of mined salt in large vacuum pan evaporators and frequently contains magnesium chloride as an impurity. The magnesium chloride is deliquescent and the absorbed water will cause the salt to cake and not run easily through shakers. To prevent this caking, small quantities of sodium bicarbonate are added to form magnesium carbonate which is not deliquescent. The addition of small amounts of sodium iodide to produce *iodized salt* has been mentioned.

Salt is an essential part of our diet, not only to make the food more palatable but to provide a source from which the hydrochloric acid in the gastric juice is produced. Salt is also present in the blood, and *physiological salt solution* containing about 0.8 per cent of sodium chloride is used medically in diluting liquids to be injected into veins. Sodium chloride is also employed as a food preservative and as a freezing mixture. Large quantities are utilized industrially in the preparation of chlorine, hydrochloric acid, and various compounds of sodium and chlorine.

9. Sodium nitrate, $NaNO_3$, is obtained from the salt deposits in Chile and is known as *Chile saltpetre*. It is used in the preparation of nitric acid, potassium nitrate and several other compounds. It has important uses as a fertilizer.

10. Sodium carbonate, Na_2CO_3, commonly called soda ash, was formerly obtained from natural deposits known as *trona*, which are found in Egypt and the United States, or by leaching the ashes of sea plants. It is now prepared from sodium chloride.

The Solvay process was introduced in 1860 by Ernest Solvay, a Belgian chemist, and is now in general use. Ammonia, carbon dioxide, salt and lime are the raw materials, and calcium chloride is the by-product. The first step of the process consists in passing ammonia and an excess of carbon dioxide into a saturated solution of sodium chloride to form ammonium bicarbonate.

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$

The ammonium bicarbonate reacts with the sodium chloride to form sodium bicarbonate which is only slightly soluble in the solution of the other salts and may be removed by filtration.

$$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$$

By repeated crystallizations a pure sodium bicarbonate may be obtained. The bicarbonate may be changed into the carbonate by heating.

$$2\ NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

If the mother liquor or filtrate is treated with calcium hydroxide the ammonia may be recovered and calcium chloride is produced.

$$2\ NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2\ NH_3 + 2\ H_2O$$

The by-product, calcium chloride, is not a valuable substance, but some quantities of it are used as a dust preventative on dirt roads.

Where electricity is cheap an electrolytic process may be used for the preparation of sodium carbonate. If a solution

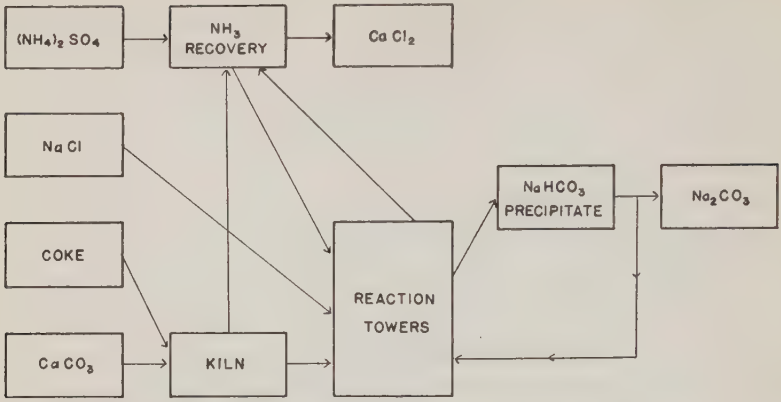


Fig. 153A. Diagram of the operations in the Solvay process.

of sodium chloride which is saturated with carbon dioxide is electrolyzed, sodium hydroxide is produced and then converted into sodium bicarbonate by the action of the carbonic acid which is present.

$$\mathbf{NaOH + H_2CO_3 \longrightarrow NaHCO_3 + H_2O}$$

This process has many advantages over the others. The carbon dioxide is produced by burning limestone which yields calcium oxide. The calcium oxide may be slaked to produce calcium hydroxide, which may be used with the chlorine from the electrolyte cell to make bleaching powder. The raw materials used in the electrolytic process are salt, limestone and water, while sodium carbonate, sodium bicarbonate, bleaching powder, chlorine, hydrogen and calcium oxide and hydroxide are produced. The necessity of having cheap power is, however, an important factor in the consideration of the use of the process.

Sodium carbonate crystallizes from solution, as the decahydrate, $Na_2CO_3.10H_2O$, which forms large monoclinic crystals in which form it is known as *washing soda* or *sal soda*. These crystals lose water to the air to form the monohydrate which

can be further dehydrated in a current of dry air or by heating to form the anhydrous salt known as *soda ash*. Sodium carbonate is used to soften water or to remove alkaline earth ions from solution because of the insolubility of their carbonates in an alkaline solution. For example:

$$Na_2CO_3 + CaSO_4 \longrightarrow \underline{CaCO_3} + Na_2SO_4$$

It hydrolyzes to produce a definite alkaline reaction.

$$Na_2CO_3 + H_2O \longrightarrow NaHCO_3 + NaOH$$

Because of this reaction the substance is often used as a base. Since alkalis remove grease it is used as a washing aid, and in the manufacture of soaps and cleaning mixtures.

11. Sodium bicarbonate, $NaHCO_3$, may be obtained directly by the Solvay process or by treating a saturated solution of the normal carbonate with carbon dioxide.

$$Na_2CO_3 + H_2CO_3 \longrightarrow 2\ NaHCO_3$$

An aqueous solution of sodium bicarbonate is alkaline because of the action of the salt with water in producing sodium hydroxide and carbonic acid.

$$NaHCO_3 + H_2O \longrightarrow NaOH + H_2CO_3$$

This slight alkaline action of the bicarbonate makes it useful as an agent for relieving excess acidity in the stomach. The principal use of the salt is in baking where it liberates carbon dioxide when it reacts with an acid. On this account, it is known as *baking soda*. *Baking powders* contain sodium bicarbonate together with a substance which acts as an acid upon solution in water so that carbon dioxide is liberated when the mixture is dissolved. Some baking powders contain potassium acid tartrate, $KHC_4H_4O_6$, while the *alum* baking powders contain anhydrous sodium aluminum sulphate, $NaAl(SO_4)_2$.

12. Sodium sulphate, Na_2SO_4, occurs naturally as *thenardite* in deposits known as "alkali flats" or "alkali lakes" in Saskatchewan, Canada and in the south-western United States. It is produced as a by-product in the manufacture of hydrochloric acid, when it is known as *salt cake*. At temperatures below 32.4°C. it crystallizes from a solution as the decahydrate, $Na_2SO_4.10H_2O$, which is known as *Glauber's salt*. The salt is used extensively in the manufacture of glass and paper, and in the refining of nickel.

National Film Board Photo

Fig. 153B. Sodium sulphate lake in Saskatchewan.

13. Sodium bisulphite and sodium sulphite. If sulphur dioxide is passed into a solution of sodium carbonate, sulphurous acid is formed and produces its acid salt with the carbonate.

$$Na_2CO_3 + 2\ H_2SO_3 \longrightarrow 2\ NaHSO_3 + H_2O + CO_2$$

If a solution of sodium bisulphite is treated with an equivalent amount of sodium carbonate normal sodium sulphite is produced.

$$2\ NaHSO_3 + Na_2CO_3 \longrightarrow 2\ Na_2SO_3 + H_2O + CO_2$$

Both the bisulphite and the sulphite are reducing agents, and are used as preservatives, in photography and as bleaching agents. Sodium sulphite is used as an anti-chlor in bleaching because chlorine in water oxidizes it to sodium sulphate.

14. Sodium thiosulphate, $Na_2S_2O_3$, is obtained by treating a hot solution of sodium sulphite with sulphur. The salt crystallizes as the pentahydrate, $Na_2S_2O_3.5H_2O$, used in photography as a fixing agent (see Chap. 41, sec. 13). The fixing solution removes the undeveloped silver salts by forming soluble complexes. Sodium thiosulphate was once called sodium hyposulphite so it is known commonly as *hypo*.

POTASSIUM

15. Occurrence. Potassium is found combined with silica in the form of feldspars and micas in volcanic rocks. The weathering of these rocks supplies a little potassium to the soil from which plants remove it to convert it to the potassium salts of organic acids. When wood is burned potassium carbonate is found in the ashes which may be leached with water and the resulting solution evaporated to form a residue known as *potash*. There are many deposits of potassium salts throughout the world, the most important being those at Stassfurt in Germany and Searles Lake in the United States.

16. Preparation of potassium. Potassium was first obtained by electrolysis in 1807 by Davy in the same manner as that by which he obtained sodium. It is made today by methods similar to those used for the latter metal, the electrolysis of potassium hydroxide or potassium chloride. Since sodium can be made more easily and cheaply and serves equally well for most purposes, the production of potassium is not extensive.

17. Properties of potassium. Potassium is very like sodium. It reacts violently with oxygen, sulphur and the halogens. The metal and its compounds impart a violet colour to a gas flame and may be detected spectroscopically by this violet light.

18. The oxides of potassium. There are two oxides of potassium as in the case of sodium. Potassium oxide, K_2O, is formed when potassium nitrate is heated with potassium in the absence of air. The oxide reacts violently with water to form the hydroxide and when exposed to the air unites with more oxygen to form the yellow peroxide, K_2O_2. As in the case of sodium the peroxide is formed when the metal burns.

19. Potassium hydroxide, KOH, is prepared electrolytically from a solution of potassium chloride, or by treating potassium carbonate with a suspension of calcium hydroxide in water. It is a deliquescent white solid which is very soluble in water. It is known commonly as *caustic potash* or *potash lye*. It absorbs carbon dioxide and forms potassium carbonate; it is sometimes utilized to remove both carbon dioxide and water from gases. Its solution is strongly basic. Since it is more expensive than sodium hydroxide, the latter is used wherever possible.

20. The potassium halides. *Potassium chloride*, KCl, is a white salt very like sodium chloride. It is generally obtained from the minerals sylvite and carnallite, the latter being a double salt of potassium and magnesium, $KCl.MgCl_2 6H_2O$. Since magnesium chloride is more soluble than potassium chloride the salts may be separated easily. Potassium chloride is used as a source of potassium compounds and as a fertilizer.

Potassium bromide, KBr, and *potassium iodide*, KI, are similar to the corresponding sodium salts. They may be prepared by adding the halogen to a hot concentrated solution of

potassium hydroxide. In the case of the bromide, the reaction is

$$6\ KOH + 3\ Br_2 \longrightarrow 5\ KBr + KBrO_3 + 3\ H_2O$$

The solution of the bromide and bromate is evaporated to dryness and heated with powdered carbon which reduces the bromate to bromide. Potassium bromide and iodide are used in preparing the silver salts used in the manufacture of photographic emulsion, and they are also used in medicine as sedatives.

21. Potassium carbonate, K_2CO_3, cannot be prepared by the Solvay process, since the bicarbonate is more soluble than ammonium bicarbonate and does not precipitate. It may be prepared from potassium chloride by heating it with magnesium carbonate, water and carbon dioxide under pressure.

$$2\ KCl + 3\ MgCO_3 + CO_2 + 5\ H_2O \longrightarrow 2\ KHMg(CO_3)_2.4H_2O + MgCl_2$$

The hydrated double salt is less soluble than magnesium chloride and may be easily separated and broken up into potassium and magnesium carbonates by heating with water at 120°C. The magnesium carbonate may be filtered off and used over again. Potassium carbonate is often obtained

Courtesy Massachusetts Experimental Station

Fig. 154. Effect of fertilizers on tomato plants. I, no fertilizer; N, nitrogen fertilizer; P, phosphorus fertilizer; K, potassium fertilizer; NP, nitrogen and phosphorus etc. All planted in poor soil.

by extraction from wood ashes. The sugar beet removes considerable potassium from the soil and after the sugar has been extracted the residue is calcined to obtain potassium carbonate. The salt is a white deliquescent powder which crystallizes from water as the hydrate, $2K_2CO_3.3H_2O$. The aqueous solution has an alkaline reaction. The substance is known commercially as *pearl ash*, and is used in the manufacture of soft soap, hard glass, and in the preparation of other potassium salts and fertilizers.

22. Potassium nitrate, or saltpetre, KNO_3, was known to the alchemists. It was essential for the manufacture of gunpowder which is a mixture of potassium nitrate, sulphur and charcoal. The introduction of smokeless powders has displaced the use of black powder, which now has a limited use for firecrackers and some forms of blasting powder. Potassium nitrate is prepared by mixing hot saturated solutions of sodium nitrate and potassium chloride. At high temperatures sodium chloride is less soluble than the other salts so that it will precipitate and may be filtered off. The removal of this salt will cause the equilibrium to shift in the direction of the right and potassium nitrate will be produced. Since it is the least soluble salt at lower temperatures it will crystallize out on cooling.

$$\mathbf{NaNO_3 + KCl \longrightarrow KNO_3 + NaCl}$$

Although it does not form a hydrate, small amounts of water are enclosed within the crystals which will break up explosively when heated. This is known as *decrepitation*. The salt is used for the manufacture of gunpowder and the curing of meat. The red colour of "corned beef" is due to the use of potassium nitrate.

23. Potassium chlorate. When an excess of chlorine is passed into a warm saturated solution of potassium hydroxide, potassium chloride and potassium hypochlorite are formed.

The potassium hypochlorite changes into potassium chlorate as soon as it is produced. These changes may be shown by the following equations:

$$3\ Cl_2 + 6\ KOH \longrightarrow 3\ KCl + 3\ KOCl + 3\ H_2O$$
$$3\ KOCl \longrightarrow 2\ KCl + KClO_3$$
$$\overline{3\ Cl_2 + 6\ KOH \longrightarrow 5\ KCl + KClO_3 + 3\ H_2O}$$

Potassium chlorate may also be made by the electrolysis of a potassium chloride solution. At slightly higher temperatures it will commence to decompose and give off oxygen. You have seen how this decomposition is hastened by the presence of a catalyst in the laboratory preparation of oxygen. Potassium chlorate is a vigorous oxidizing agent and care must be taken in heating mixtures which contain it. A mixture of potassium chlorate and sugar will take fire explosively when concentrated sulphuric acid is dropped upon it. The salt is used in the preparation of matches, and also in medicine.

24. Other potassium compounds. *Potassium cyanide* is the salt of the very weak but poisonous hydrocyanic acid. It is just as poisonous as the acid. It is deliquescent and dissolves in water to form an alkaline solution due to hydrolysis. It forms stable complex ions with a great many of the heavy metals and these are used in electroplating and metallurgy (see Chap. 41, sec. 16). *Potassium permanganate* is one of the strongest oxidizing agents and its action on hydrochloric acid, ferrous iron and sulphurous acid is described elsewhere (see Chap. 27, sec. 3 and Chap. 42, sec. 21). *Potassium dichromate*, $K_2Cr_2O_7$, is used in tanning light leathers because it makes the collagen fibres insoluble in water.

Potassium compounds are tested for by the violet colour which they give to a flame. The flame must be viewed through a thick blue glass to filter out the intense yellow colour of the ever-present sodium ion.

THE REST OF THE FAMILY

25. Lithium. The metal resembles potassium and sodium. It is the lightest of the metals, with a specific gravity of 0.534. Lithium combines directly with many elements including nitrogen and hydrogen. It reacts with water in a similar manner to potassium and sodium but the hydrogen which is produced does not take fire. The more important compounds are the chloride, bromide, carbonate and phosphate. Lithium compounds find a limited use in medicine, in the preparation of mineral waters, and in the manufacture of fireworks in which they produce a red light.

26. Rubidium. The metal resembles sodium and potassium but it is more active. Its compounds are similar to those of sodium and potassium.

27. Cesium. The metal is a liquid at temperatures above 28.5°C. and oxidizes in the air with explosive violence. Its compounds are similar to those of sodium and potassium. Cesium is used in the manufacture of radio tubes and in photo-electric cells, where its use depends on its property of emitting electrons when exposed to light.

28. Characteristics of the alkali family. The general similarities of the alkali metals and their progressive differences are shown in Table 23.

TABLE 23—COMPARISON OF PROPERTIES OF ALKALIS

Physical property	*Lithium*	*Sodium*	*Potassium*	*Rubidium*	*Cesium*
Atomic weight.....	6.94	22.997	39.096	85.44	132.91
Melting point, °C...	186	98	62.3	38.5	28.5
Boiling point, °C. ..	1220	880	760	700	670
Density.....	0.534	0.97	0.86	1.53	1.87
Specific heat.....	0.941	0.281	0.173	0.080	0.052
Flame colour	Dark red	Yellow	Violet	Red-violet	Blue
Chemical activity					
Usual valence.....	1	1	1	1	1
Action with water ..	Slow	Vigorous	Violent	Violent	Violent
Strength of base....	Strong	Strong	Very strong	Stronger	Strongest
Reducing action ...	Strong	Strong	Stronger	Still stronger	Strongest
Formula of oxides ..	Li_2O, Li_2O_2.	Na_2O, Na_2O_2.	K_2O, K_2O_2.	Rb_2O, Rb_2O_2.	Cs_2O, Cs_2O_2.

All the alkalis form strong bases, are powerful reducing agents displacing metals from their salts, decompose water liberating hydrogen, form soluble salts and all combine with hydrogen to form hydrides. In spite of these resemblances

their properties vary a little in degree from element to element as would be expected in a family.

Question Summary

1. Name the members of the alkali metal family and give their general properties.
2. How does sodium occur on the earth?
3. How is metallic sodium prepared?
4. (*a*) Give the physical properties of sodium.
   (*b*) Give the chemical properties of sodium.
   (*c*) Describe the method of spectroscopic analysis.
5. Give some uses for metallic sodium.
6. (*a*) How is sodium oxide prepared?
   (*b*) How is sodium peroxide prepared?
   (*c*) What is the chemical behaviour of sodium peroxide?
7. (*a*) How is sodium hydroxide prepared?
   (*b*) What are the properties of sodium hydroxide?
8. (*a*) Where does sodium chloride occur in the earth?
   (*b*) How is sodium chloride obtained?
   (*c*) Why is sodium chloride an important part of our diet?
9. From where does sodium nitrate come? What are its uses?
10. (*a*) Describe the Solvay process for making sodium carbonate.
    (*b*) Describe an electrolytic process for making sodium carbonate.
11. (*a*) How may sodium bicarbonate be obtained?
    (*b*) What are the chief uses of sodium bicarbonate?
12. What are the properties and uses of sodium sulphate?
13. What are the properties and uses of the sodium sulphites?
14. What are the properties and uses of sodium thiosulphate?
15. How does potassium occur on the earth?
16. How is metallic potassium prepared?
17. What are the properties of potassium?
18. Describe the oxides of potassium.
19. How is potassium hydroxide prepared? What are its uses?
20. What are the properties and uses of the potassium halides?
21. (*a*) How is potassium carbonate prepared?
    (*b*) What are the uses of potassium carbonate?
22. How is potassium nitrate prepared? What are its uses?

23. (*a*) How is potassium chlorate prepared?
(*b*) What is the chemical behaviour of potassium chlorate? Why should great care be taken in handling it?

24. Describe the preparation and properties of potassium cyanide.

25. (*a*) What are the properties of lithium and its compounds?
(*b*) What are the uses of lithium compounds?

26. What are the properties of rubidium?

27. What are the properties of cesium?

28. Describe briefly the general resemblances of the alkalis and illustrate some gradations in their properties.

Chapter 30

The Elements Are Related

1. Introduction. If you tried to learn all that is now known about each individual element and its compounds the task would be impossible of accomplishment. Fortunately as you have seen, the elements may be grouped into families which have similar properties and we can learn what is probably true about an unknown element by inference from the known behaviour of its relatives. Just as all the substances of this world, from the delicate filament of a housefly's wing to the whirling masses of the universe, are built of some ninety bricks called elements, so the elements themselves are built out of a few simple units. The first step toward the discovery of the structure of the atoms was the working out of the family tree which relates the properties of different elements.

You have learned about the early attempts to classify the elements into metals and non-metals, or base formers and acid formers, and you know that many elements behave in both ways according to conditions so the classification was not very satisfactory. Soon after Dalton had given his atomic theory to the scientific world men began to ponder the question of the relationship between the atoms. Why did they have different weights? Was there any relation between the chemical properties and the atomic weight? How many different kinds of atoms are involved in the make-up of matter? We now turn to the story of their early attempts to answer these questions.

2. Prout's hypothesis. In 1815 after the first tables of atomic weights were published, Dr. William Prout, a London physician, noticed that many of the atomic weights were multiples of the atomic weight of hydrogen. He suggested that all elements were built out of hydrogen atoms. Thus oxygen was made from 16 atoms of hydrogen, nitrogen from 14 atoms, carbon from 12 atoms and so on for all the known elements. He suggested that fractional atomic weights such as that of chlorine, 35.5, were due to errors. Dozens of chemists, such as Berzelius in Sweden and Stas in Belgium, showed by painstaking experiments that the average atomic weights determined by chemical analyses were not multiples of the atomic weight of hydrogen. For nearly 100 years the scientific world remained convinced that Prout's hypothesis was an idle fancy. He was really quite correct, because hydrogen did contain the two basic building units in the structure of matter—electrons and protons—but no techniques for proving the theory were available in his day.

3. Dobereiner's triads. About 1817 Dobereiner noticed that bromine, chlorine and iodine were as similar as identical triplets; they had the same valence, formed the same type of salts, were soluble in the same solvents and had dozens of other identical properties. In 1829 he pointed out that the atomic weights of the members of any group of three similar elements were in arithmetical progression. He called these groups of three elements *triads*, and showed that the atomic weight of the second element was the average or mean of the atomic weights of the lightest and heaviest elements in the triad. The values of those physical properties which depend on the atomic weights, such as the boiling point, melting point, specific heat, density etc., were also found to obey the rule that the three values could be placed in order so that the difference between successive values was constant. The table below illustrates this law. Intermediate values are underlined.

TABLE 24—PROPERTIES OF SOME TRIADS

Element	*Valence*	*Oxide*	*Melting point*	*Boiling point*	*Density*	*Atomic Weights*
			°C.	°C.	g./ml.	
Sulphur	2, 4, 6.	SO_2	113	445	2.07	32.06
Selenium	2, 4, 6.	SeO_2	217	690	4.47	79.2
Tellurium	4, 6.	TeO_2	451	1390	6.25	127.5
Mean of 1st and 3rd element			282	917	4.16	79.8
		Hydride				
Chlorine	1	HCl	−102	−33.7	1.42	35.46
Bromine	1	HBr	− 7.3	+58.6	3.14	79.92
Iodine	1	HI	+113	+184	4.94	126.93
Mean of 1st and 3rd element			+ 5.5	+75	3.18	81.19

4. The discovery of periodicity. After Cannizzaro made it possible to select the atomic weights in a conclusive manner and the work of Berzelius and Stas had given them precise values, John Newlands, an Englishman, realized that all the elements could be placed in order so that groups similar to Dobereiner's triads would be repeated. The rare gases of the atmosphere were not yet discovered when he arranged the elements in order of their atomic weights so he wrote down the elements *in successive rows of seven.* He called each *row* or *period* an octave because every eighth element had chemical properties similar to those of the element in the row above it. His fellow-members of the Royal Society scoffed at his "Law of Octaves" and asked him why he did not try arranging the elements in the order of their first letters. Their ridicule stopped his efforts to classify the elements but they were glad enough to give him a medal when other men

showed how great had been his insight into the relations of the elements.

Lothar Meyer in Germany plotted graphs of the properties of the elements arranged according to their atomic weights and the periodic nature of the variation was very evident as you can see from the figure below where the atomic volume is plotted against the atomic weight.

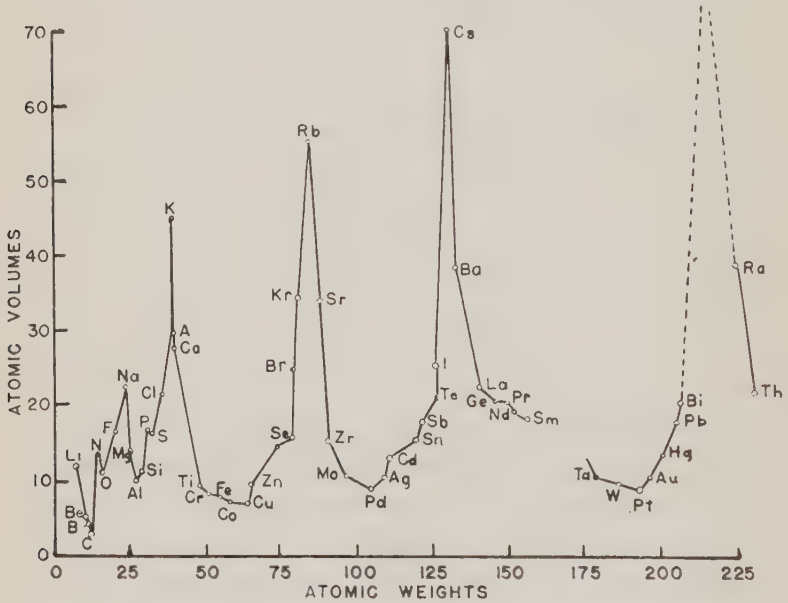


Fig. 155. Periodic changes in the atomic volumes of the elements.

This method showed that certain elements might be missing from the tables of known elements but their properties could be predicted. Many national groups give Lothar Meyer the credit for discovering the periodic law.

5. Mendeléeff's periodic table. Quite independently Dmitri Mendeléeff, in Russia, worked out a *periodic table* of the elements. He recognized that:

(1) The third and later periods were longer than the first two periods.

(2) Spaces had to be provided for undiscovered elements.

(3) Elements had to be arranged under those of similar properties even if the atomic weights were slightly out of order.

This system of classification is still one of the simplest and most convenient arrangements. His first two periods each contained seven elements and the next three periods contained seventeen elements. Since the rare gases were discovered each period now has one element more, which may be placed at the beginning of the row. Mendeléeff worked out the probable physical and chemical properties of the missing elements. He called them *eka-aluminum*, *eka-silicon* and *eka-boron* meaning like aluminum, silicon and boron respectively. He must have felt the thrill of a vindicated prophet when eka-aluminum was discovered in France in 1875 and named Gallium. Its properties were those he had predicted or they were very similar to the ones he had predicted.

TABLE 25—PREDICTION AND DISCOVERY OF ELEMENTS

Property	*Predicted* *Eka-silicon*	*Actual* *Germanium*	*Predicted* *Eka-Aluminum*	*Actual* *Gallium*
Atomic weight	72	72.60	69	69.7
Density	5.5	5.35	5.9	5.95
Melting point	. . . .	958°C.	Low	30.2°C.
Oxide	EsO_2	GeO_2	Ea_2O_3	Ga_2O_3
Atomic volume . . .	13	13.5	About 11.7	11.71

Since the chemical properties of the elements recur in every period as the atomic weight increases, Mendeléeff described the general behaviour of elements in what is called the periodic law. When any quantity, or property such as the valence, depends upon some other quantity or property such as the atomic weight the first quantity is said to be a function of the second quantity. Function simply means

"depends upon" or "varies with". Periodic means to change rhythmically. The properties of the elements ebb and flow like the tides.

The rule of behaviour of elements or the *periodic law* was stated in this mathematical language: *The properties of the elements are periodic functions of their atomic weights.* Various properties increase and decrease as the atomic weight increases.

6. A modern periodic table of the elements. We can learn some useful things from the revised form of the periodic table (Table 26).

(*i*) The horizontal rows, single or double, are called periods. There are five complete periods and the sixth is incomplete.

(*ii*) The vertical rows, which have single elements in each short period and two elements in each long period, are called *groups*. The number of a group is either one of the valences of the elements in the group or it is the number which when subtracted from *eight* will give one of the common valences. This is Abegg's Rule of Eight but it does not hold for the three sets of triads in what is called Group 8.

(*iii*) After the first two short periods each group may be subdivided into two different sub-groups or families. These are labelled A and B. The *A family elements* in this table *are characteristic* of the gradual change in properties found in the first two periods. The *B family elements* have little relation to the groups in which they are placed in the Mendeléeff type of periodic table. *They are all transition elements.* Except in some minor respects their properties are not like those of the characteristic elements.

(*iv*) The Zero Group consists of the rare gases of the atmosphere, which have no valence and no chemical properties except inertness; it therefore has no sub-groups. It has been added to Mendeléeff's table.

Table 26—MENDELEEFF'S PERIODIC TABLE (Revised 1948)

Group / Period	0	1		2		3		4		5		6		7		8		
1	2 **He** 4.003	3 **Li** 6.94		4 **Be** 9.02		5 **B** 10.82		6 **C** 12.01		7 **N** 14.008		8 **O** 16.00		9 **F** 19.00				
2	10 **Ne** 20.183	11 **Na** 22.997		12 **Mg** 24.32		13 **Al** 26.97		14 **Si** 28.06		15 **P** 30.98		16 **S** 32.066		17 **Cl** 35.457				
Family		A	B	A	B	A	B	A	B	A	B	A	B	A	B	B		
3	18 **A** 39.944	19 **K** 39.096	29 *Cu* 63.54	20 **Ca** 40.08	30 *Zn* 65.38	31 **Ga** 69.72	21 *Sc* 45.10	32 **Ge** 72.60	22 *Ti* 47.90	33 **As** 74.91	23 *V* 50.95	34 **Se** 78.96	24 *Cr* 52.01	35 **Br** 79.916	25 *Mn* 54.93	26 *Fe* 55.85	27 *Co* 58.94	28 *Ni* 58.69
4	36 **Kr** 83.7	37 **Rb** 85.48	47 *Ag* 107.88	38 **Sr** 87.63	48 *Cd* 112.41	49 **In** 114.76	39 *Y* 88.92	50 **Sn** 118.7	40 *Zr* 91.22	51 **Sb** 121.76	41 *Cb* 92.91	52 **Te** 127.61	42 *Mo* 95.95	53 **I** 126.92	43 *Ma*	44 *Ru* 101.7	45 *Rh* 102.91	46 *Pd* 106.7
5	54 **Xe** 131.3	55 **Cs** 132.91	79 *Au* 197.2	56 **Ba** 137.36	80 *Hg* 200.61	81 **Tl** 204.39	57 *La* 138.92 58-71 *Rare Earths*	82 **Pb** 207.21	72 *Hf* 178.6	83 **Bi** 209.0	73 *Ta* 180.88	84 **Po** 210	74 *W* 183.92	85 **Ab?**	75 *Re* 186.31	76 *Os* 190.2	77 *Ir* 193.1	78 *Pt* 195.23
6	86 **Rn** 222	87 **Vi?**		88 **Ra** 226.05			89 *Ac*	90 *Th* 232.12		91 *Pa* 231		92 *U* 238.07			93 *Np*	94 *Pu*	95 *Am*	96 *Cm*

Man-made elements

Elements 90-96 appear to be part of a new series like the rare Earths (Actinide series).

(*v*) Hydrogen cannot be satisfactorily included in this type of periodic table.

(*vi*) The properties of the elements in the two different families of any one group may be very different. This is because one sub-group is characteristic of the elements above it in the two short periods, while the other sub-group consists of transition elements. The transition elements can have only a slight resemblance to the group (see Chap. 32, sec. 7). For example, the only similarity between the A and B families of Group I is that the A family or alkali metals: lithium, sodium, potassium, rubidium and cesium, always have a positive valence of 1; while in the B family: copper, silver and gold, only silver is regularly monovalent. Another similar feature is that they are all called metals, but otherwise they are quite dissimilar.

(*vii*) There are some exceptions to the periodic law based on atomic weights. If the elements are placed strictly according to their atomic weights, potassium comes after chlorine and is followed by argon. This would place potassium in the Zero Group with helium and neon and put argon in Group I with sodium and lithium. The properties of an element are thus the most important factor in deciding its position in the table. If you examine the table carefully you will find two other cases where an element of lower atomic weight has to be placed after an element of higher atomic weight because of physical and chemical properties.

(*viii*) There were other peculiarities about the table which could only be understood after the internal structure of atoms was surmised:

(1) Group 8 was different from other groups.

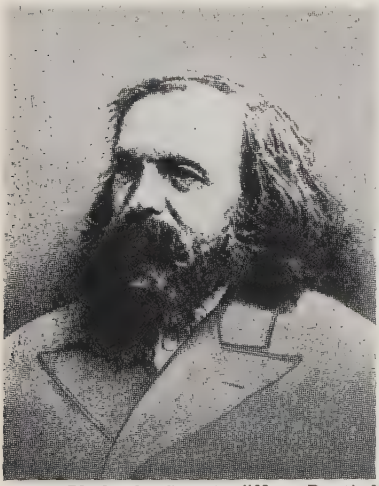
(2) There were fourteen elements starting with element 58 which did not fit into the table.

(3) There was a tendency for the metals to be arranged in the left-hand side of the table with the non-metals appearing

in the right-hand corner. This was spoiled by the distribution of the transition elements such as manganese, chromium, vanadium, molybdenum, copper, and the Group 8 metals along the various groups.

(*ix*) In any period, the elements of the A sub-groups show a gradual transition from a very metallic element, whose oxide forms a strong base in water, to a very non-metallic element.

(*x*) The old periodic system was useful because it grouped similar elements together, predicted missing elements, and provided a basis for understanding the structures of the atoms as they became known.



From Black & Conant: "New Practical Chemistry", courtesy The Macmillan Company

Fig. 156. Dmitri Ivanovitch Mendeléeff (1834-1907). A Russian chemist who arranged the elements according to their atomic weights.

From Ewing Galloway and courtesy Museum of Science and Industry

Fig. 157. The international character and world-wide usefulness of the periodic table is shown by this exhibit.

7. Periodic properties of the characteristic elements. (A family elements).

(*i*) *Changes in valency.* It is more informative to discuss the changes in valency toward hydrogen and oxygen. If

certain metals do not form hydrides they form very similar compounds with methyl radicals (CH_3) where the radical behaves like hydrogen. The following table shows the compounds for the first two periods with the valences. You will notice that the valence increases or decreases by one unit as you pass from group to group and that the sum of the positive and negative valences in groups 4, 5, 6 and 7 equals eight.

TABLE 27—VALENCE OF ELEMENTS IN PERIODS

Group	0	1	2	3	4	5	6	7
Period 1	He	LiH	$Be(CH_3)_2$	BH_3	CH_4	NH_3	H_2O	HF
Period 2	Ne	NaH	$Mg(CH_3)_2$	$Al(CH_3)_3$	SiH_4	PH_3	H_2S	HCl
Valence to H_2	0	1	2	3	4	3	2	1
Period 1	He	Li_2O	BeO	B_2O_3	CO_2	N_2O_5	—	—
Period 2	Ne	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Valence to O_2	0	1	2	3	4	5	6	7
Sum of valences to H_2 and O_2	—	—	—	—	8	8	8	8

(*ii*) *Changes in metallic behaviour.* When an oxide unites with water it forms a hydrated oxide. Some hydrated oxides yield hydroxyl radicals in solution so we call them *hydroxides*. The soluble ones produce large numbers of hydroxyl ions in solution; therefore we call them *bases*. Other hydrated oxides yield more hydrogen ions than hydroxyl ions in solution so we call them *ternary acids*. Those which will yield hydroxyl ions in the presence of an acid and yield hydrogen ions in the presence of a base are called *amphoteric hydroxides* (see Chap. 23, sec. 5). The basicity or acidity of a hydrated oxide depends upon the degree of

Table 28—BEHAVIOUR OF SOME HYDRATED OXIDES IN WATER

Group	1		2		3		4		5		6		7	
Form / Period	Basic	Acidic	Basic	Acidic	Basic	Acidic	Basic	Acidic	Basic	Acidic	Basic	Acidic	Basic	Acidic
1	LiOH		$Be(OH)_2$	H_2BeO_2	$B(OH)_3$	H_3BO_3		H_2CO_3		HNO_2 HNO_3				
2	NaOH		$Mg(OH)_2$		$Al(OH)_3$	$HAlO_2$		H_2SiO_3		H_3PO_3 H_3PO_4		H_2SO_3 H_2SO_4		$HClO_3$ $HClO_4$
3	KOH		$Ca(OH)_2$						As_2O_5	H_3AsO_3 H_3AsO_4		H_2SeO_4		$HBrO_3$ $HBrO_4$
4	RbOH		$Sr(OH)_2$				$Sn(OH)_2$ $Sn(OH)_4$	H_2SnO_2 H_2SnO_3	$[Sb(OH)_3]$ $SbOCl$	$[H_3SbO_3]$ $[H_3SbO_4]$	$[Te(OH)_4]$ $Te(OH)_6$	H_2TeO_3 H_2TeO_4		HIO_3 HIO_4
5	CsOH		$Ba(OH)_2$				$Pb(OH)_2$	$[H_2PbO_3]$ $[H_2PbO_4]$	$Bi(OH)_3$	$HBiO_3$				
General Behaviour	Strongly Metallic		Metallic		Weakly Metallic		Mostly Amphoteric		Weakly Non-metallic		Mainly Non-metallic		Strongly Non-metallic	

Notes: Transition elements are exceptions. [ ] indicates problematic existence.

metallic behaviour shown by the element. If the hydrated oxide tends to behave predominantly as a hydroxide we indicate this by writing the metal symbol followed by the formula for the hydroxide, e.g., NaOH. If it behaves distinctly as an acid we write its formula as that of an acid with the hydrogen first and showing the element as part of a non-metallic radical, e.g., $HAlO_2$. Amphoteric hydroxides should be written both as acids and bases. This has been done in the following table where the more common formulation is underlined. You will note that the amphoteric hydroxides are along a diagonal strip from beryllium to bismuth.

Metallic behaviour increases with the atomic weight in any group while *non-metallic behaviour increases with atomic weight along any period.* The periodic table of hydrated oxides (Table 28) shows the seven characteristic groups and omits the rare gases.

(*iii*) *Changes in physical properties of elements and compounds.* As you have seen in Tables 22 and 23 the physical properties of the elements of a family suffer a gradual transition from element to element. The same is true of the physical properties of their oxides, chlorides, sulphides, carbonates, nitrates, sulphates and all their other compounds. This made it possible to predict the properties of all the compounds of an unknown element as well as those of the element itself. There are some abnormalities but the general pattern is one of gradual change. The melting and boiling points and the densities generally increase with increasing atomic weights but the solubility may change in either direction. The important thing to note is that *the properties of an element or a compound can be estimated with considerable accuracy if it can be placed in its family of elements.* The formulas of its compounds are immediately known and their physical characteristics can be deduced.

8. Forms of the periodic table. You will find a great many forms of the periodic table. Each emphasizes some important feature of this great generalization.

(*a*) The spiral form illustrates the fact that the rare gases come between the beginning and the end of each period and shows that the flat form is only a cylindrical arrangement divided vertically either before or after the rare gases.

(*b*) An expanded form shows the Zero group and the first two A families on the left side of the transition elements or the B families, and the remainder of the A families on the other side. Since the ten elements from scandium to zinc are all transition elements, the same as the ten from yttrium to cadmium, this arrangement shows each period as a single row with the transition elements between the metals and the non-metals.

(*c*) There are various forms based on the electronic structure of the atoms. These forms usually fit hydrogen and helium into the scheme as a very short period of two elements. They also show why the fourteen rare earth elements must be fitted into Group III. These forms will be more meaningful when you have studied in more detail the electronic structure of atoms (Chap. 32).

9. Application of periodic table to oxygen-sulphur group. Because oxygen and sulphur have been discussed in Chaps. 5, 14 and 20, it is convenient to mention only their family characteristics here. They have two other members in their family, selenium and tellurium, which are less abundant and less well known. With the sulphur family, as with the halogens, we find a gradual alteration of physical properties and a similarity in chemical compounds. With increasing atomic weight there is an increase in the melting point and boiling point of the elements. The same gradual increase is shown by many of their compounds. Table 29 shows some of these variations.

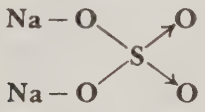
All except oxygen have valences of 2, 4 and 6. In the divalent state we have them as the negative part of oxides, sulphides, selenides and tellurides such as H_2O, H_2S, H_2Se, H_2Te. With the exception of water these hydrogen compounds are colourless gases with disagreeable odours. They form similar salts as Na_2O, Na_2S, Na_2Se, Na_2Te.

In the quadrivalent state we find O_3 or $O.O_2$, SO_2, SeO_2 and TeO_2 and the acids H_2SO_3, H_2SeO_3 and H_2TeO_3. There is no corresponding oxygen compound.

Oxygen does not have a valence of 6 but the others form SO_3, SeO_3 and TeO_3 as well as H_2SO_4, H_2SeO_4 and their corresponding salts. Tellurium is too metallic to form the free acid but some of the salts of the acid are known.

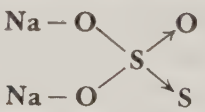
The compounds of selenium and tellurium are less stable than those of oxygen and sulphur. They are also more metallic. Selenium is amphoteric but tellurium is distinctly metallic and resembles zinc.

Oxygen and sulphur are so similar to one another that they appear to be able to replace one another in almost all compounds. We name compounds where sulphur replaces oxygen with the oxygen type of name using the prefix *thio* to indicate that sulphur replaces oxygen. For example:



sodium sulphate

Na_2SO_4



sodium thiosulphate

$Na_2S_2O_3$

Another example is the cyanate and thiocyanate

$$Na-O-C\equiv N \quad \text{and} \quad Na-S-C\equiv N$$

Oxygen is a stronger non-metal than sulphur and when it is available in high concentrations it can replace sulphur in its binary compounds.

$$2\ ZnS + 3\ O_2 \longrightarrow 2\ ZnO + 2\ SO_2$$

We could make parallel lists to illustrate the similarity between the compounds of oxygen and sulphur with the metals. Many of these have been mentioned in previous chapters but they are collected together in the table for convenient comparison.

TABLE 29—PERIODIC PROPERTIES OF THE OXYGEN-SULPHUR FAMILY

Property	*Oxygen*	*Sulphur*	*Selenium*	*Tellurium*
Atomic weight	16.00	32.06	78.96	127.61
Melting point	−218.4	112.8	200	452
Boiling point	−183.0	444.6	688	1390
Density	1.43 g./l.	2.07	4.8	6.24
Colour of vapour	Nil	Brown	Deep red	Yellow
Colour of solid	Blue	Yellow	Black	White
Hydride	H_2O, H_2O_2	H_2S	H_2Se	H_2Te
Stability of hydride	Most stable	Stable	Unstable	Very unstable
Oxides	$O.O_2$	SO_2, SO_3	SeO_2, SeO_3	TeO, TeO_2 TeO_3
Strength of "ous" acid	....	Weak	Very weak	Nil
Strength of "ic" acid	....	Strong	Moderate	Weak
Arsenic compounds	As_2O_3 As_2O_5	As_2S_3, As_2S_5	As_2Se_3	As_2Te_3
Copper compounds	Cu_2O, CuO	Cu_2S, CuS	CuSe	CuTe
Iron compounds	FeO, Fe_2O_3 Fe_3O_4	FeS, FeS_2, Fe_2S_3	FeSe, Fe_2Se_3	FeTe, Fe_2Te_3
Lead compounds	PbO, Pb_3O_4 PbO_2	PbS, $PbSO_4$	PbSe, $PbSeO_4$	PbTe, $PbTeO_4$
Silver compounds	Ag_2O	Ag_2S, Ag_2SO_4	Ag_2Se, Ag_2SeO_4	Ag_2Te, Ag_2TeO_4
Sodium compounds	Na_2O, Na_2O_2	Na_2S, Na_2S_2	Na_2Se,	Na_2Te,
Tin compounds	SnO, SnO_2	SnS, SnS_2	SnSe,	SnTe,
Zinc compounds	ZnO.	ZnS.	ZnSe.	ZnTe.

The application of the periodic law to the other groups of elements in the table will be made in the several chapters devoted to them. The remaining metals of the A families or characteristic sub-groups will be treated in the next topic along with the remainder of the non-metals. The metals of the B families or transition groups will be treated in Topic 7. The study of the metals and non-metals is thus based on this periodic classification of the elements.

Question Summary

1. (*a*) How does the periodic table serve us in the study of chemistry?
(*b*) What was the earliest method of classifying elements?

2. (*a*) "Prout's Hypothesis was based on Dalton's early atomic theory." Explain this.
(*b*) Why was Prout's hypothesis rejected?

3. Select a group of three similar elements from the table and illustrate Dobereiner's law of triads.

4. (*a*) Explain why Newland's Law of Octaves was not accepted in its original form.
(*b*) Point out the most evident repetitions of properties which occur in the first two octaves of Newland's arrangement.
(*c*) Describe briefly the magnitude and general trend of the atomic volumes of the elements from boron to iron.
(*d*) Would you expect the variations in density and boiling points to be like the variations in atomic volume?
(*e*) What generalization can you make about the physical properties of the transition elements?

5. (*a*) What principles made Mendeléeff more successful than Newlands?
(*b*) Explain how Mendeléeff predicted the properties of unknown elements.
(*c*) State the periodic law in its older form and give, in your own words, the meaning of the statement.

6. (*a*) Explain the meaning of the following terms: short period, group, long period, family, Abegg's Rule of Eight, transition elements and zero group.
(*b*) State clearly, in regard to the periodic table in this book, the reason for assigning an element to:
(*i*) the A family or Sub-group A;
(*ii*) the B family or Sub-group B.
(*c*) Would you expect the A and B families of a group to be very similar? Why?

(*d*) Name six elements which are not placed in the table in order of their atomic weights.

(*e*) Why are they placed in inverse order?

(*f*) Name some peculiar regularities of the table which are best explained by electronic structure.

(*g*) Describe very generally the transition which occurs in chemical properties along any period of the table.

(*h*) What are the most important uses of the periodic classification of the elements?

7. (*a*) Illustrate how the valency toward hydrogen changes in the characteristic elements of any period. Compare this with the changes in valency toward oxygen.

(*b*) How are hydroxides related to the oxygen acids? Illustrate how the metallic behaviour of the characteristic elements alters with increasing atomic weight.

(*c*) How does metallic behaviour change with atomic weight in any family of characteristic elements?

8. Look up some other form of the periodic system and prepare a report on its merits and limitations.

(Hint: Try other textbooks in Chemistry or issues of *Journal of Chemical Education*.)

9. (*a*) Describe the gradual change in properties found in the oxygen-sulphur family.

(*b*) Illustrate the similarities in properties among the members of the oxygen-sulphur family.

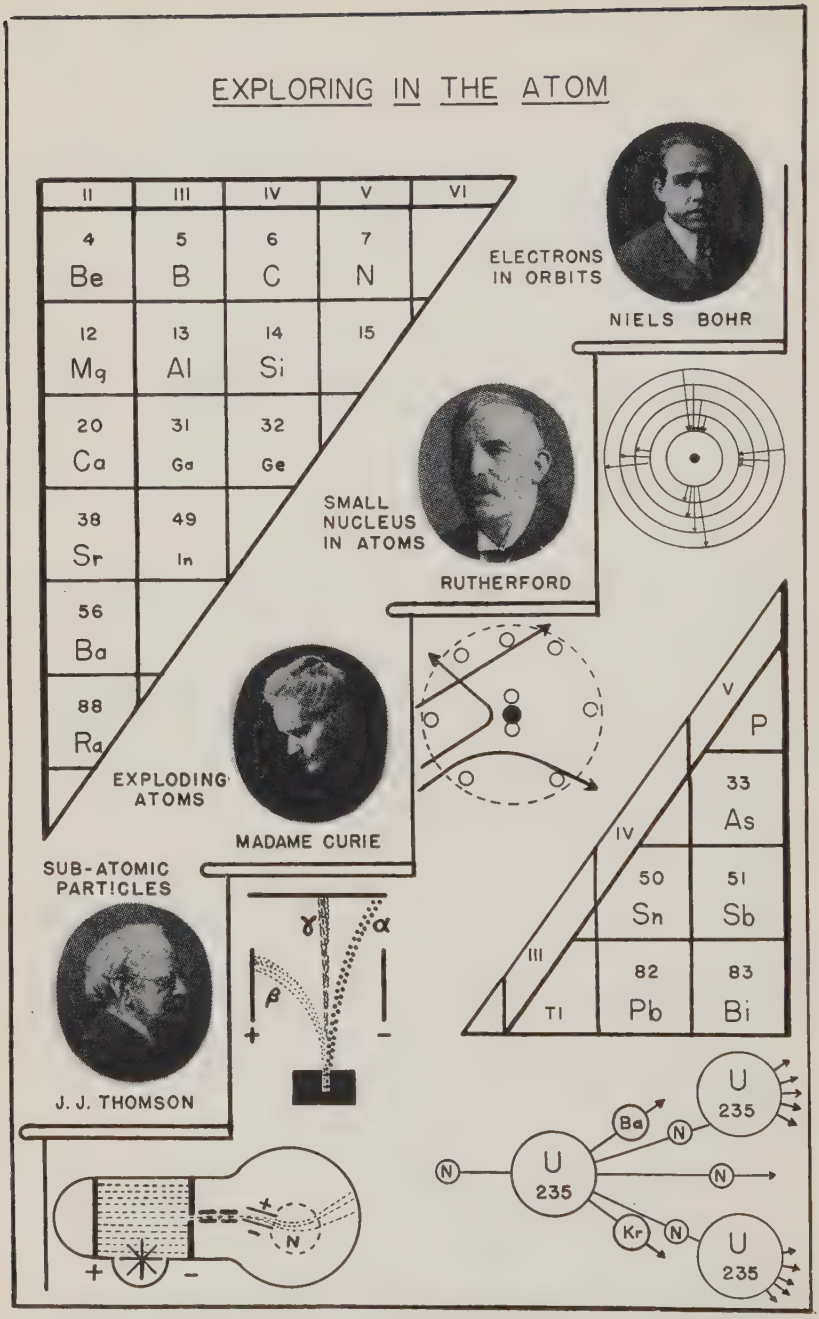
(*c*) Discuss the similarity in the chemical behaviour of the elements oxygen and sulphur.

Topic Six

EXPLORING IN THE ATOM

When men had learned that all the objects of the world were made of some ninety elements which could be classified into families they said, "Surely these invisible atoms must be built of units." Although nineteenth-century chemists disproved Prout's theory and said that the alchemical transmutations were impossible they carefully examined the generation of X-rays, the spectra of coloured light from heated elements, the discharge of electricity through rarified gases and the spontaneous decomposition of the radio-active atoms.

In this careful searching they found wonderful evidence of the existence of electrons, protons, neutrons and other sub-atomic particles within atoms. They found that atoms could be transformed into other atoms, that the particles in hydrogen were in all atoms and that the nucleus of certain atoms could be caused to explode by a nuclear chain reaction. These discoveries have caused the twentieth century to be called "the atomic age."


EXPLORING IN THE ATOM
II
III
IV
V
VI
4
Be
5
B
6
C
7
N
12
Mg
13
Al
14
Si
15
20
Ca
31
Ga
32
Ge
38
Sr
49
In
56
Ba
88
Ra
ELECTRONS IN ORBITS
NIELS BOHR
SMALL NUCLEUS IN ATOMS
RUTHERFORD
EXPLODING ATOMS
MADAME CURIE
SUB-ATOMIC PARTICLES
J. J. THOMSON
γ
α
β
+
−
N
V
P
33
As
IV
50
Sn
51
Sb
III
82
Pb
83
Bi
Tl
U
235
Ba
Kr
N

Chapter 31

The Pathway into a New World

1. Introduction. In Chap. 15, we took a quick glance at what men have come to believe about the architecture of atoms. We mentioned that these beliefs were due to the work of scientists in those branches of physics where subatomic particles are studied. It would be well for us to examine these remarkable discoveries a little more closely in order to appreciate how it is possible to arrive at such miraculous opinions about the insides of particles which are only about 0.00000001 cm. (10^{-8} cm.) in diameter, when no man can see into them with any kind of a microscope.

Three types of investigation established the electronic concept of structure. Work on the conduction of electricity through gases led to the discovery of X-rays and the electron. Work on radioactivity led to techniques for studying and counting particles and work on the spectra of elements made possible the investigations into the arrangement of electrons in atoms. We will now try to get a brief view of these developments.

2. Conduction of electricity through gases. Sprengel invented a vacuum pump, Volta and his followers provided a source of high potential electricity, and in 1859 Plucker discovered that gases at very low pressures will conduct a current of electricity.

Sir William Crookes devised ingenious methods to demonstrate that the discharge of electricity through the gas was due to particles travelling at a high velocity. He showed that they would cast shadows, turn a tiny paddle wheel,

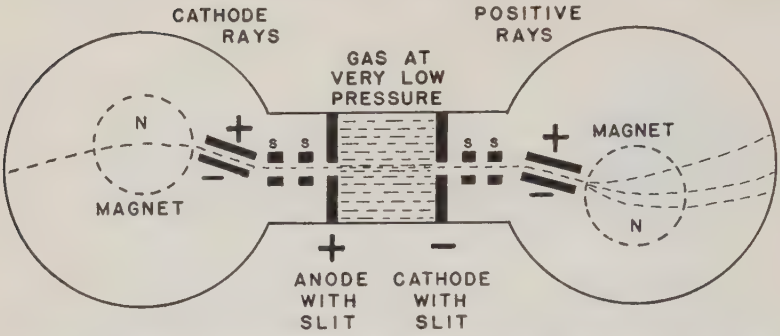
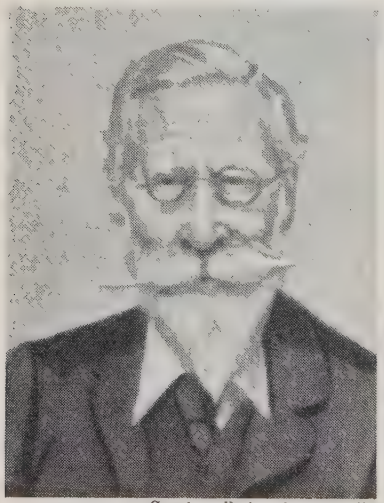


Fig. 158. Cathode rays are streams of electrons and positive rays are the charged atoms. Both are deflected by magnetic and electrostatic fields.

and proceeded from the negative pole or cathode. They have since been called *cathode rays* because they tend to leave in a direction at right angles to the cathode. Crookes suggested that they carried an electric charge and Perrin proved that it was a negative charge by deflecting them in electric and magnetic fields.



Courtesy Fisher Scientific Co.

Fig. 159. Sir William Crookes (1832-1919), an English chemist and physicist, investigated electrical discharges in evacuated tubes.

Courtesy The Bettman Archive

Fig. 160. Wilhelm Konrad Roentgen (1845-1923), a German physicist, discovered X-rays.

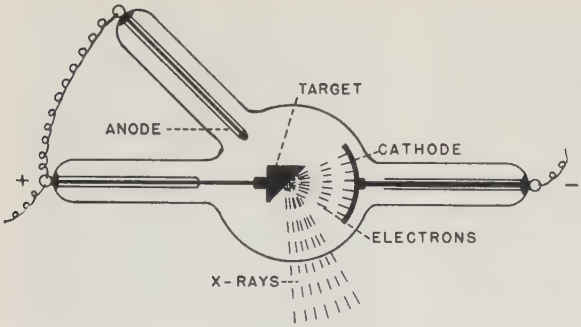


Fig. 161. X-rays are produced when high-speed electrons strike a metal.

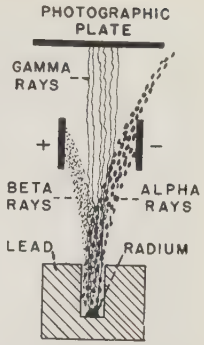


Fig. 162. Electrically charged plates used to show the three types of radium rays.

In 1891 G. J. Stoney suggested that the particles of negative electricity be called *electrons* and Sir J. J. Thomson measured the ratio of the charge, e, to the mass, m, for the cathode ray particles. He found the ratio, e/m, to be the same regardless of the gas in the tube or the metal of the electrodes. It appeared as if *these particles could be derived from all elements* and that cathode rays were streams of electrons. Twenty years later Robert Millikan determined the value of the charge, e, so from e/m the mass of the particle was then calculated to be 1/1838 of the mass of the hydrogen atom.

In 1886 Goldstein used a discharge tube with a hole in the cathode and found rays behind the cathode *going away from the positive pole.* These were investigated and found to be *rays of charged atoms.* These are now called *gaseous ions* or *positive rays* (see Fig. 158). It was soon postulated that they were produced by the removal of one or more electrons from neutral atoms.

In 1895 Roentgen observed that a screen of zinc sulphide would glow in a dark room if it was near one of these discharge tubes. He then placed the discharge tubes near photographic plates which were still sealed in black wrappers.

The films were darkened as if exposed to light. These invisible radiations were called X-rays or Roentgen rays. They are produced when high-speed electrons from the cathode strike the material of the anode (see Fig. 161).

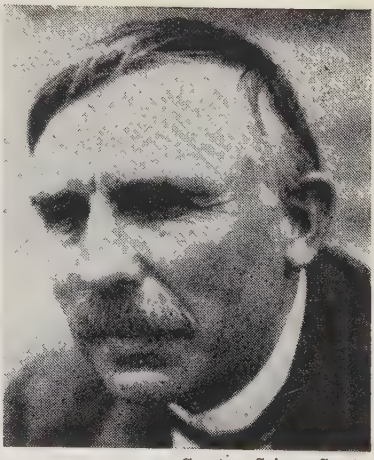
3. Radioactivity. In 1896 Becquerel observed the same kind of mysterious fogging of photographic plates in their light-proof cartons when certain phosphorescent minerals were placed near them. Such minerals continue to glow in the dark after exposure to bright sunlight and he thought they might continue to give out invisible rays for some time. A uranium mineral was found to give off invisible penetrating rays even when not exposed to the sunlight. He found that all uranium salts gave these rays in proportion to their content of uranium. The rays would ionize the air and cause the charge on an electroscope to leak off in proportion to the quantity of uranium and its distance from the electroscope. Materials which give out such rays are said to be radioactive.

Mme. Curie studied with Becquerel and found that thorium minerals would also give out radiation. The amount of radiation from pitchblende was greater than would be expected from its uranium content. It was suspected that an unknown element was present. In an epic work of personal sacrifice, endurance and faith, Pierre and Marie Curie finally isolated two new and strongly radioactive elements, *radium* and *polonium*. Radium was similar to barium and by innumerable meticulous crystallizations Mme. Curie obtained a few crystals of radium bromide from several tons of ore. It was only a few milligrams but it was enough to prove the isolation of a new element.

Radium salts were found to glow continuously in the dark and emit enough heat every minute to melt about an equal weight of ice. The scientific world was startled by this spontaneous emission of energy without chemical reaction. Apparently it would continue indefinitely and could be neither

From Black & Conant: "New Practical Chemistry", courtesy The Macmillan Company

Fig. 163. Madame Curie (1867-1934) and her daughter Madame Joliot (1897-) each received a Nobel prize for work in radioactivity. Madame and Pierre Curie prepared the first crystals of radium.



Courtesy Science Service

Fig. 164. Sir Ernest Rutherford (1871-1937), a British physicist, studied the transmutation of elements and established the idea of the atom having a very small nucleus.

stopped, slowed down nor increased by any known means. To explain this Rutherford and Soddy postulated in 1902 that radioactive atoms disintegrate or break apart into atoms of lower atomic weight, setting free this atomic energy. The techniques which had been used to study the particles in discharge tubes were now applied to these rays or emanations from radioactive substances. A part of the beam of rays from polonium or radium would travel straight ahead in a magnetic or electric field like X-rays or light waves. These were called *gamma* (γ) *rays* and they are like X-rays of very short wave length. Another part of the beam is deflected toward a positive plate and is found to be a stream of electrons. These are called *beta* (β) *rays*. A third part is deflected slightly in the opposite direction and these are called the *alpha* (α) *rays* (see Fig. 162). We can count alpha particles by the spots of light they give on a fluorescent screen and

measure the charge on any number of particles. They are found to have a double positive charge. By measuring the ratio of charge to mass, e/m, we find the mass is four times the mass of the hydrogen atom or equal to that of the helium atom. The spectroscope has been used to show that helium is produced by neutralizing these alpha particles with electrons. They are thought to be helium atoms with a double positive charge.

4. Evidence for empty spaces in atoms. The alpha particles have enough energy to penetrate several inches of air or thin sheets of gold or aluminum. C. T. R. Wilson showed that the path of a particle may be photographed in air which is saturated with moisture by a sudden drop in pressure. The pressure drop makes the air supersaturated and the excess moisture will condense around dust particles or ions. If sub-atomic particles strike molecules of air they will knock electrons out of them to produce ions which act as condensation nuclei, and the distance a particle travels will be measured by its *fog track* (see Fig. 165).

The kinetic theory and Avogadro's number may be used to calculate the number of molecules in the measured thickness of air or the number of atoms in the thin sheet of metal. The calculation reveals that an alpha particle may pass through over a hundred thousand atoms before it is stopped. It is quite often deflected slightly, sometimes sharply deflected, but seldom stopped. We know metals are incompressible and we believe the atoms in them are in close contact with one another so the *alpha particles must be passing through the atoms themselves.*

Lord Rutherford, working at McGill University in Montreal and later in England, measured the scattering of these alpha particles and calculated the amount of empty space in atoms. Fig. 166 shows the principle of the experiment. The atom was calculated to have a *positively charged nucleus* less than

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Fig. 165

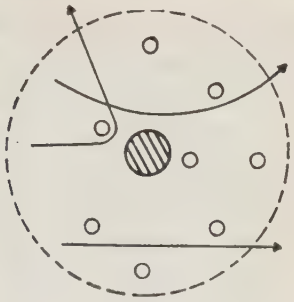

Fig. 166

Fig. 165. Fog tracks of alpha particles passing through nitrogen. The particle on the left struck a nitrogen nucleus.

Fig. 166. Alpha particles are repelled by the positive nucleus if they approach it too directly.

3×10^{-12} cm. in diameter or only 1/1000 as large as a hydrogen atom. The diameter of the electron is believed to be only about one-tenth that of the nucleus. From the scattering experiments Rutherford calculated that the nucleus had a positive charge less than half its atomic weight.

The physical evidence so far presented is summed up in what is called the Rutherford Atom. It is visualized as a very minute positively charged nucleus surrounded by the number of electrons required to produce a neutral whole. The weight of the atom is almost entirely due to the nucleus and the volume is due to the orbits of the electrons. Further work has revealed details of the arrangement of the electrons and the nature of the particles in the nucleus.

5. The nucleus. X-ray studies by H. G. J. Moseley, a brilliant young English physicist killed at Gallipoli during World War I, showed that the wave length of the X-rays was

dependent upon the atomic weight of the element in the target. When a plot of this wave length relationship was examined it also suggested a *unit increment of positive charge from atom to atom.* This was found to be equal to the rank the elements would have when arranged in order of increasing atomic weights. It became possible to give all the atoms a number according to the order of the increasing positive charges on their nucleii. These numbers were called the *atomic numbers.*

The atomic numbers place the elements in order of their complexity of structure: hydrogen is 1, helium is 2, lithium is 3, and thus through all the elements to uranium, number 92. It was found that the elements which are out of the normal order of property changes by atomic weights in the periodic system, such as potassium and argon, were in the proper order when the charge on the nucleus was determined. A more accurate statement of the periodic law could be made. *The properties of the elements are periodic functions of their atomic numbers.*

The most logical way to add weight and positive charge in uniform units is to assume the existence of a particle with a weight equal to hydrogen and a positive charge of the same magnitude as that carried by an electron but of opposite sign. One of these units makes the nucleus of a hydrogen atom. These positive units are called *protons.*

When certain light atoms such as lithium or beryllium are exposed to alpha particles a new particle of unusual penetrating power is produced. It is not deflected by electric or magnetic fields because it has no charge. It has the same mass as a proton and is believed to be either a characteristic particle or a close association of a proton and an electron. It is called a *neutron.*

Although neutrons and protons are thought to be the fundamental constituents of atomic nuclei other particles

such as the positron (positive electron) and the mesotron (heavy electron) have been proposed, and alpha particles may be present in many atons. As yet there is no complete picture of the structure of the nucleus.

6. Isotopes. A careful study of the positive ions of pure elements revealed that all the atoms are not identical in atomic weight as Dalton had assumed. Lithium has two kinds of atoms, one of them has an atomic weight of six and the other has an atomic weight of seven. Such *atoms with similar chemical properties but different atomic weights are called isotopes.* The number of electrons outside the nucleus is the same for both atoms but they differ in the number of neutrons in the nucleus. This is shown in Fig. 82 (see Chap. 15, sec. 7).

The fractional values found for atomic weights could now be explained. Chlorine is found to have two isotopes of mass number 35 and 37. These are present in the proportion of 77.2 per cent of the former and 22.8 per cent of the latter in all samples of chlorine whether elementary or compound. These values account for the chemical atomic weight being a fractional value and show that Prout's hypothesis was fundamentally correct but lacking in detail. In 100 mols of chlorine we have $(77.2 \times 35) + (22.8 \times 37) = 3545.6$ g. This gives an average atomic weight of 35.456.

An instrument for separating the isotopes with great precision was developed by Aston and in any of its many forms is called a *mass spectrograph.* With its aid the number and weight of the isotopes of each of the elements has been determined. The principle is shown in Fig. 158.

7. The composition of atoms and gaseous ions. Atoms are thus believed to have a nucleus of very small volume made up of protons and neutrons. The weight of the atom is almost entirely in the nucleus and is equal to as many units as the number of protons and neutrons. The positive charge on the nucleus is equal to the number of protons. The posi-

tive charge is equal to the atomic number or order number of the element.

To have a neutral atom there must be as many electrons outside the nucleus as there are free protons in the nucleus. These are called *planetary electrons* and the outermost ones are called *valence electrons*. The volume of the atom is the space required by these extra-nuclear or planetary electrons. Electrons are removed when struck by very high-speed particles and the part which remains is a positive ion because it is short one or more electrons.

The voltage between two electrodes in a tube of gas at low pressure regulates the energy with which electrons leave the cathode. No glow occurs in the tube until a certain voltage is reached, but as the voltage is increased this glow will disappear, and it will reappear again at a higher voltage value. Further increases in voltage produce similar results but the increases become smaller and smaller until a value is reached beyond which all voltages cause the glow to continue. This value is the *ionization potential*. To understand these stepwise changes it was necessary to revise our ideas of the nature of energy. Niels Bohr introduced the idea that energy is added to atoms not continuously but in *quanta* or units of energy. The interpretation of these results is that the voltage must give an electron from the cathode sufficient speed to penetrate an atom and disturb its outermost electron. The electron goes to what is called a *higher energy level* when it receives a quantum or unit of energy and the atom is now said to be an *excited atom*. This is by analogy with our human experiences when our ways of life are disturbed. The electron is thought to be more easily disturbed to higher energy levels after the initial boost. A voltage is finally reached where the electron is completely removed (see Fig. 167).

After an electron has been removed from an atom a much higher voltage is needed to remove a second electron because

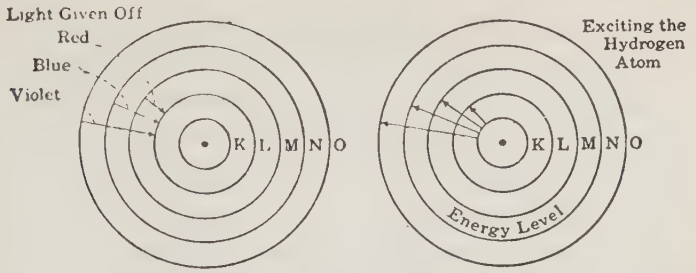

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Fig. 167. An excited atom radiates light as the displaced outer electrons fall back to lower energy levels. Electrons are excited to higher energy levels by light, heat, electron bombardment, etc.

it is removed against the attraction of the excess positive charge already on the ion.

8. The emission of light by atoms. Combustion is often accompanied by the production of light and a great deal is known about the nature of light itself. We know that the energy depends upon the frequency and that higher frequencies go with shorter wave lengths. The same is true of radio waves and sound waves. Men learned how to measure the wave length of visible light by means of prisms and diffraction gratings in instruments known as *spectroscopes and spectrographs.* These are described in textbooks of physics.

When the idea of energy levels in atoms was proposed the origin of radiant energy became apparent. If energy is absorbed in moving an electron to a higher energy level in an atom it must be *emitted when an electron falls back to a lower energy level.* If the energy is radiated with a frequency of vibration within the range of the visible spectrum we will have the emission of visible light. This is shown in Fig. 167.

The eye sees certain frequencies of radiation as particular colours and most atoms have some transition between energy levels which will give a visible colour. You are familiar with the red glow of neon, and you may have seen the green glow due to one of the many energy level transitions in excited

mercury atoms. The yellow light emitted by sodium enables us to detect minute traces of the element. Calcium gives an orange-yellow colour to the flame while lithium and strontium give a bright red colour. Potassium gives the flame a violet colour and some of the transition metals give dozens of lines in the visible spectrum. Copper is one of those with the largest variety of possible transitions giving frequencies in the visible region. "Yule logs" are made by soaking used paper in copper sulphate and salt. This gives the more volatile copper chloride and when the copper atoms are volatilized into the flame of the fireplace they are excited by the heat energy. When the electrons start to fall back to their normal places in the atoms they emit green and blue light in an intriguing variety of shapes and shades.

9. The arrangement of electrons in atoms. Calculations based upon accurate measurements of the frequency of such emitted light have enabled scientists to determine how the electrons are arranged about the nucleus. The rule is that any energy level cannot have more than $2n^2$ electrons, where n is the order number of the level from the nucleus. The first level or electron shell, K, around the nucleus can accommodate a maximum of two electrons (2×1^2), the second level, L, can have between one and eight (2×2^2) electrons, the third, M, from one to eighteen, and so on. Electron levels seldom fill up to the maximum number of eighteen or thirty-two electrons unless there are other shells beyond them at least partly completed.

Question Summary

1. What three types of investigation established the electronic concept?

2. (*a*) How did the study of Crookes' tubes contribute to our knowledge of the structure of atoms?

(*b*) How did the discovery of positive rays advance our knowledge of gaseous ions?

(*c*) How are X-rays produced?

3. (*a*) What are radioactive materials?
(*b*) How were radioactive materials discovered?
(*c*) Describe briefly the discoveries of Mme. Curie.
(*d*) Explain the nature of α, β, and γ rays.

4. (*a*) How are these invisible particles traced?
(*b*) Describe the contribution of Lord Rutherford and his associates to our ideas of atomic structure.

5. (*a*) What is the origin of the atomic number?
(*b*) State the periodic law in modern terms. How is the modern statement better than the original statement in terms of atomic weights?
(*c*) What are protons? What are neutrons?

6. (*a*) What are isotopes? Explain with a diagram.
(*b*) Explain why many chemical atomic weights have fractional values.
(*c*) How are the isotopes of an element determined?

7. (*a*) How are protons and neutrons related to the following? (*i*) Nuclear charge; (*ii*) Atomic weight; (*iii*) Atomic number; (*iv*) Alpha particles.
(*b*) How are the planetary electrons related to the following? (*i*) Nuclear charge; (*ii*) Volume of the atom; (*iii*) Atomic number; (*iv*) Valence electrons; (*v*) Gaseous ions; (*vi*) Excited atoms.

8. (*a*) Why do elements emit visible radiation?
(*b*) How can elements be excited to emit radiation? Give some common examples.

9. State the rule about the maximum number of electrons in the various energy levels of atoms.

Chapter **32**

The Answer to Many Riddles

1. Introduction. Hope springs eternal in the heart of the chemist. He always hopes to explain why some atoms are metallic and some non-metallic; why some form ions by themselves, others only as radicals, and some do not form ions at all. He likes to know why elements fall into groups of similar elements, why they unite with one another only in certain ratios and why some of them spontaneously dissociate. He seeks reasons for the variable valence of certain elements and for their differences in ability to displace hydrogen from acids as well as many other properties.

The value of the electron theory of atom structure lies in its ability to offer satisfying explanations of these varied phenomena. By picturing the atom as a planetary system of electrons around a positive nucleus it applies the rule of maximum stability to the changes made by the system. This is the rule that every substance tends to get into the state of minimum available energy just as water runs downhill until it reaches the lowest level. The state of minimum available energy is the state of maximum stability. As you know, the water can only be removed from the oceans by putting energy into it to vaporize or lift it to a higher level as a gas.

2. Inert gas structures. The electron arrangement found in the inert gases appears to represent the condition of lowest available energy for atoms. An examination of the structures of helium, neon, argon, krypton, xenon and radon in Table 30 of sec. 7 will enable you to see that their *outer shells* contain either *two electrons*, in the case of helium, or *eight electrons* in

all the others. An outer shell of eight electrons is thus taken to be a stable and inert structure with practically no chemical activity. It will also be observed that all the shells or energy levels in the inert gases contain completed groups of two, eight, eighteen or thirty-two electrons.

The chemical activity of other elements is believed to be due to a tendency toward the realization of inert gas structures. The inert gases have very high ionization potentials and are apparently in a condition of minimum available energy for the electrons which make up the external structure of atoms. It appears that *all atoms react in such a manner as to attain a structure similar to that of the inert gas nearest to them in the periodic system.* This gives them some of the stability of the inert gas structures.

3. Valence. Two methods for attaining an inert gas structure are available to atoms.

(1) an atom may gain or lose outer electrons (see Fig. 168A).

(2) Atoms may pool or share their outer electrons (see Fig. 168B).

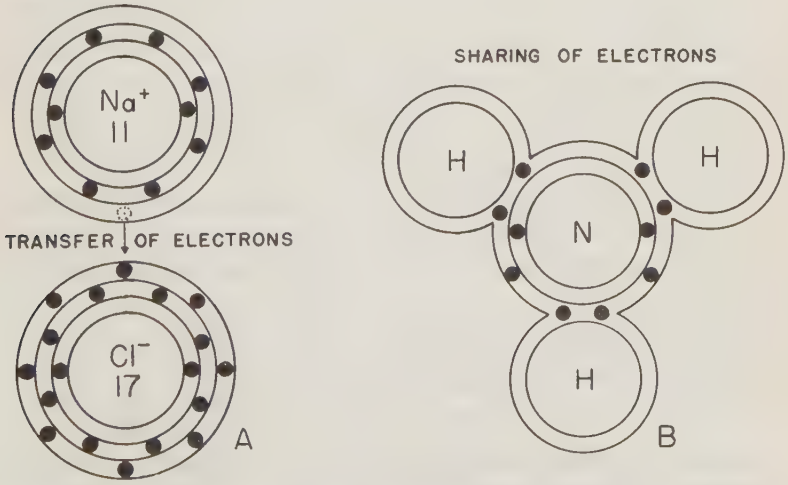


Fig. 168. Two methods by which atoms can attain an inert gas structure.

Nature usually chooses the process which involves the least expenditure of energy. Atoms which can achieve inert gas structures by the loss or gain of one or two electrons use this device when electrons are easily transferred. This leaves them with an excess of positive or negative electricity and *they attract other atoms by means of their electric charges. They are electrovalent.* When atoms cannot readily transfer electrons to other atoms they may acquire more stable arrangements by sharing electrons. They co-operate in using pairs of electrons to complete the electron shells of both atoms. The atoms are held together by their shared electrons in a state of minimum available energy. *When atoms are combined by the sharing of a pair of electrons they are said to be covalent.* Some atoms can show both electrovalence and covalence according to conditions.

4. Metals and metal ions. We have represented the lithium atom as having three electrons. Two of these electrons are in an inner stable shell like those of the helium atom; but there is one electron in a shell which will eventually hold eight electrons. The easiest way for lithium to achieve a structure like helium is to give away its outer electron. This will give it a positive charge because it has only two electrons left and the nucleus has a positive charge of three. It is a lithium ion with a valence of one. Lithium has a very strong tendency to give up electrons in this way to form positive ions. It is thus said to be very metallic. If we examine the electron structures of the elements which follow the inert gases in Table 30, we will see that they can all achieve inert gas structures by the loss of electrons. If we look in the electrochemical series in Chap, 38. sec. 6, we will see that these are also the most active metals.

We may explain the ability of metals to conduct electricity by the ease with which they will pass along electrons. A number of electrons are shoved in at one end of a metallic

conductor by an electrical pressure, an equal number shoved out at the other end. Since like charges repel each other most of this passing along of electrons will be done by the surface atoms.

The outer electrons of sodium and potassium are so readily lost that a quantum of light falling on the clean metal surface will knock out an electron. This is the principle of the photo-electric cell. Some metals and metallic oxides even lose electrons when heated by an electric current and they are used as filaments in radio tubes. The current is carried across the tube by the electrons thrown out of the metallic filament and replaced from the radio circuit which carries them from the positive plate back to the filament.

The loss of electrons from the transition elements or B family elements seldom leaves them with 2, 8, or 18 electrons in the outer shell. This enables them to lose different numbers of electrons according to the conditions of the reaction. We say they have a *variable valence*. Copper and silver, for example, can lose one electron and have a shell of eighteen electrons exposed. This outer electron is easily lost and these metals are excellent conductors of electricity. The metals with variable valence which have less than eighteen electrons in the outer shell after the valence electrons are lost will have opportunities for the oscillation of electrons between levels and sub-levels in their atoms. This enables many of them to absorb and emit visible light of specific wave length so they form *coloured ions*. The cupric ion has 17 electrons and when attached to water molecules it is a blue colour. Similarly ferric ions are orange, cobalt ions are pink and nickel ions are green when they are hydrated. The electron structures of some metal ions are shown in Fig. 169.

This enables us to answer the first riddle. *Metals are elements which tend to lose electrons from their outer shells to form positive ions or cations.* When an element behaves as a metal

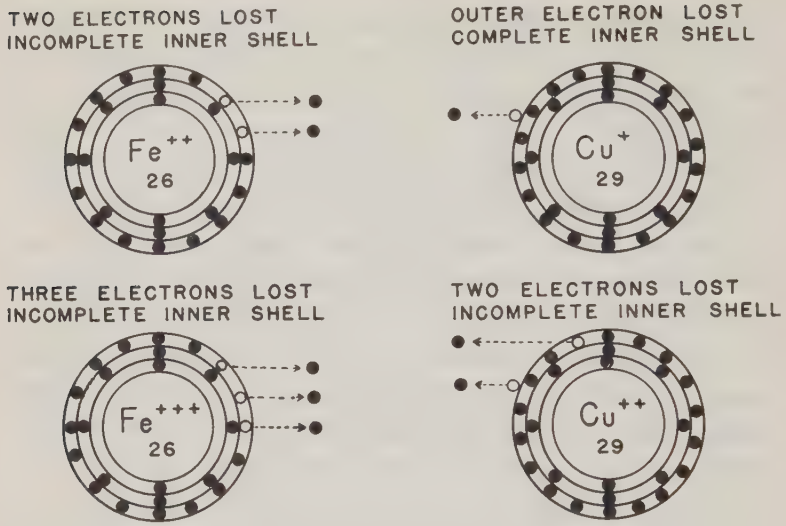


Fig. 169. Electron structures of some metal ions.

it has a positive electrovalence equal to the number of electrons it is able to lose to other elements or radicals.

5. Non-metals and polar compounds. If you will examine the structures of fluorine, oxygen, chlorine, sulphur, bromine, iodine and other elements which come just before the inert gases you see that they lack only one or two electrons to complete outer shells. They will tend to *gain electrons* and to hold on tightly to the electrons they already possess. This will give them more electrons than protons so they become *negative ions*. In general this process only extends to the gaining of one or two electrons.

In the free state of the element the electrons in the outer shell are so tightly bound that these substances are good electrical insulators; for example, sulphur. Even elements with only four electrons such as silicon have their electrons tightly bound and compounds of silicon and oxygen are also good insulators. Even the silicon compounds with the metals, such as are found in glass and porcelain, are familiar electrical insulators.

If a metal and a non-metal are brought into suitable proximity the metal atom may lose its electron or electrons to form a positive ion and the non-metal atom may gain an electron or electrons to form a negative ion. The resulting ions will attract one another to form an *electrovalent* or *polar compound*, so called because of the oppositely charged ends of the ion pair. The formation of such a polar compound is illustrated diagramatically in Fig. 83 (see Chap. 15, sec. 8).

The metal with the greatest tendency to give up electrons will be the most active metal or the strongest reducing agent because it will give its outer electron to metal ions which are less active and thus reduce them from ions to the free metal. The farther an electron is from the positive nucleus the more easily it is lost. Thus potassium is more active than sodium in losing electrons. Lithium is somewhat of an exception to the general rule. The voltage values given in the electrochemical series are a measure of the tendency of atoms to give their outermost electrons to other atoms.

The non-metal with the greatest attraction for electrons will be the strongest oxidizing agent. The closer the electrons can come to the positive nucleus the more tightly they are held so fluorine is the strongest oxidizing agent among the elements.

We can thus explain such riddles as the relative activity of metals and non-metals, the formation of ions in solid crystals, the conduction of electricity, the formation of coloured ions and many other behaviourisms of matter.

6. Covalence and non-polar compounds. Atoms with more than one or two electrons may only *share* them with other atoms so electrons shells of two or eight electrons are possible for all of them. Carbon is the most familiar example. It has four electrons outside of a shell of two electrons. It must acquire four electrons or part with four electrons to have the structure of neon or helium. The electrons are too

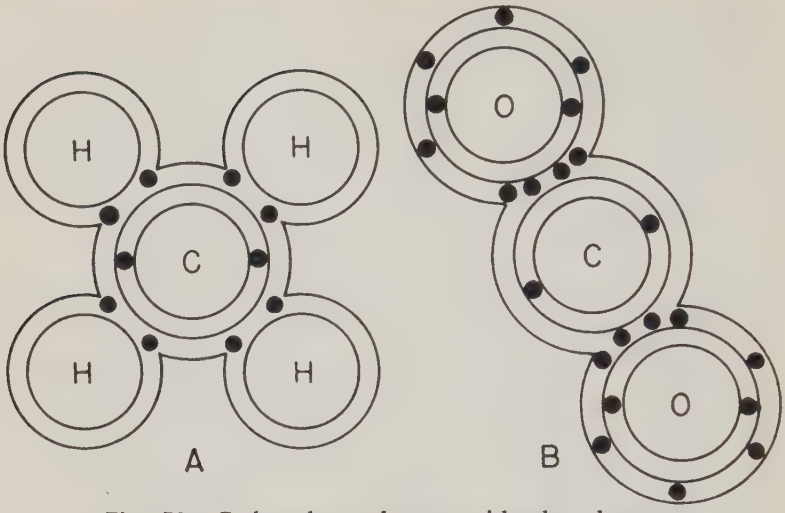
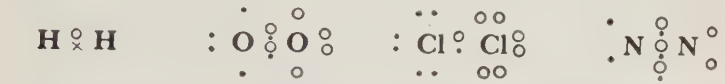


Fig. 170. Carbon shares electrons with other elements.

tightly bound to be lost so it *shares* them with other elements to form covalent bonds. If it shares its four electrons with four hydrogen atoms it forms methane as shown in Fig. 170A. No ions are produced in this type of compound formation and *the molecules have no definitely charged parts* so we call these *non-polar compounds*. The shared electrons are usually those of the outermost energy level and we may use the schematic method of representation proposed by G. N. Lewis. The nucleus and all the electron shells under the valence shell are represented by the symbol of the element. The part of the atom which is not active in chemical changes is called the *kernel*. The electrons of the outermost shell are represented by dots, crosses, or small circles to distinguish those from different atoms. Thus sodium may be Na·, Ca:, aluminum Al:, fluorine :$\ddot{\underset{\cdot\cdot}{\text{F}}}$·, oxygen :$\ddot{\underset{\cdot\cdot}{\text{O}}}$, etc. We can represent the formation of carbon dioxide in the very simple manner shown in Fig. 170B. The carbon atom has four electrons which it shares equally with two oxygen atoms having six electrons in their outer shells. The oxygen atoms

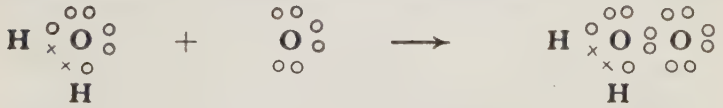
each yield to the carbon atom a share in two of their own electrons. The carbon atom now has at least a share in eight electrons and each oxygen atom also has a share in a similar number. This arrangement must enable all three of these atoms to reduce their available energy because carbon dioxide is a very stable substance.

By this concept we can understand Avogadro's discovery that the elementary gases occur in diatomic molecules such as H_2, O_2, N_2, Cl_2. These atoms may gain stability in the inert gas structures made possible by the sharing of electrons. Two hydrogen atoms have enough electrons for a helium shell; two oxygen atoms can each have a neon shell by sharing two electron pairs; and two chlorine atoms can have argon structures by sharing one pair. Some of these are shown below.



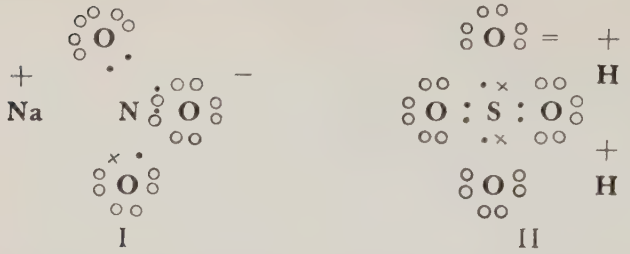
The inert gases are all monatomic because they already have inert gas structures.

In the cases so far described the atoms have contributed one electron each to the formation of the electron pair. Sometimes one of the atoms will furnish *both the electrons for the electron pair*. It thus becomes a donor while the other atom which takes the pair of electrons to complete its octet is an acceptor. This type of covalence is called *co-ordinate covalence*. The formation of hydrogen peroxide illustrates this type.



Water Oxygen Hydrogen peroxide

Negative radicals are usually held together by covalent bonds but one element has also acquired electrons so the whole group has a negative charge.



In I, the nitrogen atom could receive an electron from sodium to give it a total of six electrons and a negative charge of one. It could then form a double covalent bond with one oxygen atom so as to give each of them an octet. It would then have two pairs of electrons which it could *donate* to each of two more oxygen atoms to complete their shells of eight. Often arrows indicate that these are co-ordinate covalent bonds. The compound as a whole is a polar compound due to the electrovalent bond but the radical alone is a covalently bonded unit which behaves as a single atom. Electronic theory thus clears up many of the mysteries of valence and molecular structure.

7. The periodic system. Atoms made of a positive nucleus and successive shells of electrons can be used to explain the properties of all the elements of the periodic system. Table 30 shows the atomic numbers of the elements above the symbols and the number of electrons in the outer shells below the symbols. We shall first try to learn the structures and then how transition elements, rare earths and periodic properties arise from the changes in structure which take place from element to element.

(*i*) *Hydrogen* consists of *a proton* surrounded by *one electron.*

(*ii*) *Helium* has an atomic weight of four and it is element number two. The nucleus is equivalent to *two protons* for atomic number two, and it has *two neutrons.* It will have *two electrons* which can be held in the first shell.

(*iii*) *Lithium* with an atomic weight of seven and an atomic number of three will have a nucleus equivalent to *three protons* and *four neutrons*. This requires *three electrons*, two in the first shell and one in a new shell.

(*iv*) *Beryllium* with an atomic weight of nine and an atomic number of four has a nucleus equivalent to *four protons* and *five neutrons*. Two of the *four electrons* will be in the second shell. You can apply these methods to each of the isotopes of the elements in the first period of the table since isotopes have whole number atomic weights. This will complete the second shell with the element *neon* which has eight electrons in its outer shell (see Fig. 81, page 206).

(*v*) *Sodium* with an atomic weight of twenty-three and an atomic number of eleven could have the equivalent of *eleven protons and twelve neutrons* in its nucleus. Two of the *eleven electrons* could be in the first shell, eight in the second shell, and one in a new shell which is the valence shell. Sodium is thus similar to lithium in having one outer electron in its valence shell. The other elements of this period have progressively more electrons in the third shell up to a maximum of eight. An atom does not fill up valence shells to eighteen electrons so this period ends with *argon*.

(*vi*) *Potassium* with an atomic weight of thirty-nine is the nineteenth element. The nucleus could be *nineteen protons and twenty neutrons* and the *nineteen electrons* may be two in the first shell, eight in the second, eight in the third, leaving one electron for a fourth shell, so potassium is very much like sodium. Calcium will have two electrons in this fourth shell to make it similar to magnesium.

(*vii*) *Transition elements* begin to appear after calcium as the third shell starts to fill up from eight to eighteen electrons. The number of electrons in the valence shell of these transition elements will be less than the number of the group into which the element happens to fall in the periodic distribution

TABLE 30—ARRANGEMENT OF OUTER ELECTRONS IN ELEMENTS

Group / Period	0	1		2		3		4		5		6		7		8		
1	2 **He** 2,	3 **Li** 2, 1		4 **Be** 2, 2		5 **B** 2, 3		6 **C** 2, 4		7 **N** 2, 5		8 **O** 2, 6		9 **F** 2, 7				
2	10 **Ne** 2, 8	11 **Na** 2, 8, 1		12 **Mg** 2, 8, 2		13 **Al** 2, 8, 3		14 **Si** 2, 8, 4		15 **P** 2, 8, 5		16 **S** 2, 8, 6		17 **Cl** 2, 8, 7				
		A	B	A	B	A	B	A	B	A	B	A	B	A	B	B		
3 All 2, 8,	18 **A** −8	19 **K** −8, 1	29 ***Cu*** −18, 1	20 **Ca** −8, 2	30 ***Zn*** −18, 2	31 **Ga** −18, 3	21 ***Sc*** −9, 2	32 **Ge** −18, 4	22 ***Ti*** −10, 2	33 **As** −18, 5	23 ***V*** −11, 2	34 **Se** −18, 6	24 ***Cr*** −11, 3	35 **Br** −18, 7	25 ***Mn*** −13, 2	26 ***Fe*** −14, 2	27 ***Co*** −15, 2	28 ***Ni*** −16, 2
4 All 2, 8, 18	36 **Kr** −8	37 **Rb** −8, 1	47 ***Ag*** −18, 1	38 **Sr** −8, 2	48 ***Cd*** −18, 2	49 **In** −18, 3	39 ***Y*** −9, 2	50 **Sn** −18, 4	40 ***Zr*** −10, 2	51 **Sb** −18, 5	41 ***Cb*** −12, 1	52 **Te** −18, 6	42 ***Mo*** −13, 1	53 **I** −18, 7	43 ***Ma*** −13, 2	44 ***Ru*** −15, 1	45 ***Rh*** −16, 1	46 ***Pd*** −18
5 2, 8, 18, 18 and 2, 8, 18, 32	54 **Xe** −8	55 **Cs** −8, 1	79 ***Au*** −18, 1	56 **Ba** −8, 2	80 ***Hg*** −18, 2	81 **Tl** −18, 3	57-71 Rare Earths (18-32)	82 **Pb** −18, 4	72 ***Hf*** −10, 2	83 **Bi** −18, 5	73 ***Ta*** −11, 2	84 **Po** −18, 6	74 ***W*** −12, 2	85 **Ab?** −18, 7	75 ***Re*** −13, 2	76 ***Os*** −14, 2	77 ***Ir*** −17, 0	78 ***Pt*** −17, 1
6 2, 8, 18, 32	86 **Rn** −18, 8	87 **Vl?** −18, 8, 1		88 **Ra** −18, 8, 2			89 ***Ac*** −18, 9, 2		90 ***Th*** −18, 10, 2		91 ***Pa*** −18, 11, 2		92 ***U*** −18, 12, 2		93	94	95	96

Man-made elements,

Elements 90-96 appear to be part of a new series like the Rare Earths (Actinide Series).

as electrons are drawn down to complete the third shell. Ten such transition elements will occur in each long period and three of these will be the elements of Group VIII. In the first long period the transition begins with scandium and ends with zinc which has just ten electrons more in the third shell than calcium (see Table 30).

(*viii*) *Rare earths.* The fourth shell will fill out to thirty-two electrons in two stages. In the second long period the fourth shell fills out from eight to eighteen electrons; but when the third long period begins a fifth shell starts to form. This permits the fourth shell to fill out from eighteen to thirty-two electrons and gives us the fourteen rare earth elements that have two outer shells of very similar structure but differ in the number of electrons in the fourth shell (see Table 30).

It now appears as if some of the heavier radioactive elements and the man-made elements are similar to the rare earths except that the fifth shell is expanding from eighteen to thirty-two electrons instead of the fourth shell.

(*ix*) *Sub-levels* within the major energy levels are required in order to explain *all* the known facts. These do not alter the above explanations but only give a more detailed picture. For this reason they are not indicated in the table.

The reason for the periodic repetition of properties in each sub-group now becomes apparent. *The elements of any sub-group have similar outer electron shells.* All the inert gases have outer shells of eight electrons except helium which can have a complete outer shell with only two electrons. All the alkali metals have one electron outside a shell of eight electrons except lithium which has one electron outside of a complete inner shell of two electrons. The alkali earths all have two electrons outside of a shell of eight electrons except beryllium which has a helium-like kernel. The halogens all have a shell of seven electrons outside completed shells of two, eight or eighteen electrons. Oxygen, sulphur,

selenium, tellurium and polonium all have six electrons outside the completed shells and the nitrogen-phosphorus family has five electrons outside inert gas shells. We have chosen to designate as *A families* those which have *valence shells outside of completed inner shells.* For the A families the number of electrons in the valence shell of any element is equal to the number of the group in which the element occurs. *Since chemical properties depend primarily on the number of electrons in the valence shell* elements with identical valence shells will have similar properties.

The reason for the variable valence of the *transition elements* lies in the fact that they have *incomplete shells inside the valence shell.* We have designated such elements as belonging to the *B families* or B sub-groups of the periodic system because they seldom have the number of electrons in the valence shell the same as the group number. If you examine the electron structures given for these elements in Table 31, you will note that they represent not more than one of the valences possessed by any transition element. One or more of the electrons from the expanding shell can be transferred to the

TABLE 31—ELECTRON STRUCTURES OF TRANSITION ELEMENTS

Element	*Structure*	*Valences*	*Compound*
	2, 8, 13, 1	0	metal
Cr.	2, 8, 11, 3	3	Cr_2O_3
(24)	2, 8, 8, 6	6	CrO_3
	2, 8, 13, 2	2	$MnCl_2$
	2, 8, 12, 3	3	Mn_2O_3
Mn	2, 8, 11, 4	4	MnO_2
(25)	2, 8, 9, 6	6	K_2MnO_4
	2, 8, 8, 7	7	$KMnO_4$
Fe	2, 8, 14, 2	2	FeO
(26)	2, 8, 13, 3	3	Fe_2O_3
Cu	2, 8, 17, 2	2	CuO
(29)	2, 8, 18, 1	1	Cu_2O

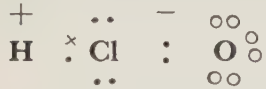
valence shell to give the element other valences. The above electron structures show how some of the transition elements acquire variable valences.

8. Variable valence. There are two reasons for the variable valence of elements.

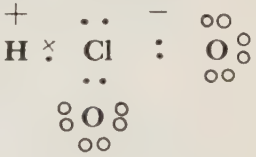
(*i*) The number of electrons in the valence shell of the transition elements may be varied. They can show variable electrovalence.

(*ii*) The number of atoms held by covalent bonds may vary according to conditions.

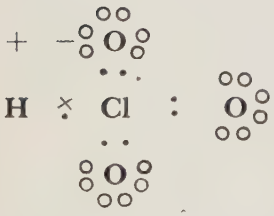
Variable electrovalence has been described in the preceding section and here is an example of variable covalence.



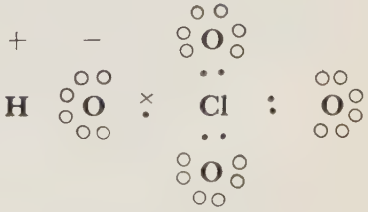
Cl = +1,



Cl = +3.



Cl = +5



Cl = +7

The valence of chlorine increases as the number of atoms held by co-ordinate covalence is increased. In each of these examples chlorine has seven valence electrons and acquires another to complete its shell of eight electrons. This gives the whole radical a negative electrovalence of one.

9. Oxidation and reduction. Reduction was originally the term used to describe the removal of oxygen from a compound (see Chap. 6, sec. 7). It was soon extended to any

reaction where the positive valence of an element was decreased. In electrolysis reduction occurs at the cathode where the positive ions are reduced to atoms as:

$$Na^{+} \longrightarrow Na;\ Ca^{++} \longrightarrow Ca;\ Zn^{++} \longrightarrow Zn$$

It is not necessary that the process proceed far enough to give the free metals as in $Fe^{+++} \longrightarrow Fe^{++}$. When the electron theory of valence was established it became evident that the reduction in valence was due to the gain of electrons. This even applied to the formation of non-metal ions from non-metals. For example, using $\underline{e}$ for electron:

$$Cl_2 + 2\underline{e} \longrightarrow 2\ Cl^{-}$$
$$Br_2 + 2\underline{e} \longrightarrow 2\ Br^{-}$$
$$I_2 + 2\underline{e} \longrightarrow 2\ I^{-}$$

Oxidation first referred to the union with oxygen. It was soon realized that the union of a substance with any non-metal was oxidation. The positive valence of a metal is increased by oxidation as when copper combines with oxygen or antimony with chlorine. This increase in positive valence

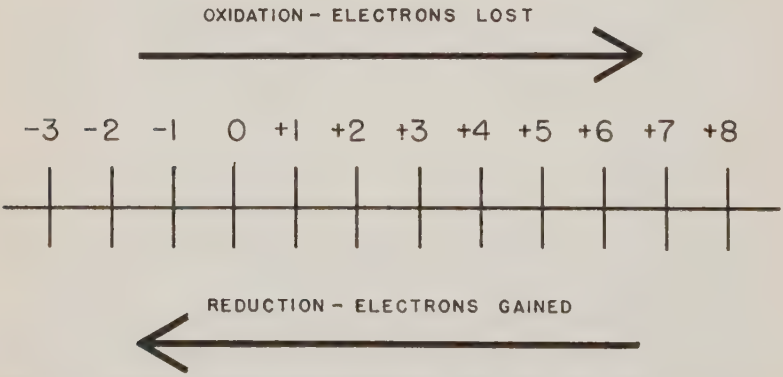


Fig. 171. Positive valence is increased by the loss of electrons and decreased by the gain of electrons.

on the electron theory is due to a loss of electrons so when a halide ion is converted to the free halogen it is a process of

oxidation, the element is shifted to the right in the valence scale (see Fig. 171). *Oxidation is an increase in positive valence caused by the loss of electrons* and the electron structures enable us to see why it is possible for an atom or an ion to suffer oxidation. Outer electrons are removed or used in the process of oxidation. For example:

$$\mathbf{Cu\ (2,\ 8,\ 17,\ 2)} \xrightarrow{-2\underline{e}} \mathbf{Cu^{++}\ (2,\ 8,\ 17)}$$

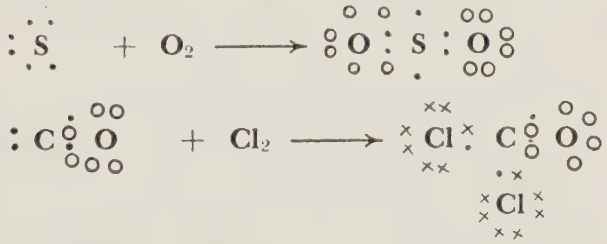
$$\mathbf{Cl^{-}\ (2,\ 8)} \xrightarrow{-\underline{e}} \mathbf{Cl^{\circ}\ (2,\ 7)}$$

Reduction is a decrease in positive valence caused by a gain of electrons. The electrons are taken up by the more oxidized form to lower the net positive charge. For example:

$$\mathbf{Fe^{+++}\ (2,\ 8,\ 13)} \xrightarrow{+\underline{e}} \mathbf{Fe^{++}\ (2,\ 8,\ 14)}$$

$$\mathbf{S\ (2,\ 8,\ 6)} \xrightarrow{+2\underline{e}} \mathbf{S^{=}\ (2,\ 8,\ 8)}$$

The oxidation of covalent elements consists in forming more covalent bonds by the actual addition of non-metal atoms such as oxygen, sulphur, chlorine, etc. For example:



Carbon monoxide + chlorine ⟶ phosgene.

This fulfils the basic idea of the word oxidation, especially where oxygen is added. Reduction in covalent compounds is the actual removal of covalently bonded elements from compounds or radicals.

When atoms are added to covalent elements electrons are rendered unavailable for further bond formation and the positive valence is increased in the same manner as if electrons had been removed. When atoms are removed from combination with covalent elements electrons are made available for bond formation and the positive valence is reduced in the same manner as if electrons had been added to the outer shell. The definitions of oxidation and reduction in terms of the loss and gain of electrons are valid for both electrovalent and covalent compounds.

Question Summary

1. What are some of the questions which find explanation by the electron theory of structure?

2. (*a*) Write the electronic structures of the inert gases.
(*b*) Why do we think other elements seek to arrange their electrons in the same manner as those of the inert gases?

3. Describe and give examples of two methods by which an atom may secure an electron arrangement like that of the nearest inert gas.

4. (*a*) Why do the metals behave as cations? Illustrate your answer with examples.
(*b*) How does the electron theory account for
(*i*) electrical conductivity of wires;
(*ii*) photoelectric effect?
(*c*) How can we explain the variable electrovalence of the transition elements?

5. (*a*) Why do non-metals tend to form anions?
(*b*) Why are non-metals good electrical insulators?
(*c*) Explain the formation of polar compounds.
(*d*) What does the electrochemical series tell us about the ease with which electrons are lost by metals?

6. (*a*) What is meant by the term covalence?
(*b*) Draw diagrams to show the electronic linkages in CH_4, NH_3, H_2O and CO_2.
(*c*) How is the diatomicity of the elementary gases accounted for by the electronic theory?
(*d*) What is the difference between co-ordinate covalence and ordinary covalence? Give examples of both.
(*e*) The ternary acids may show all types of valence in the same molecule. Give an example of this.

7. (*a*) What is peculiar about the electronic structures of the elements of a single sub-group or family? Give one or more examples.

(*b*) Trace the changes both in the units of weight in the nucleus and in electronic distribution from sodium to argon.

(*c*) What peculiarity of electronic structure is shown by the transition elements or those labelled as B sub-group elements?

(*d*) Explain the chemical similarity of the rare earth elements.

(*e*) Give examples of how the transition elements may give rise to variable electrovalences.

8. (*a*) Describe two reasons for variable valence.

(*b*) Give examples of how covalent elements show variable valence.

9. (*a*) Define oxidation and reduction in terms of electrons.

(*b*) Explain how covalent elements suffer oxidation.

(*c*) Explain how electrovalent elements suffer reduction.

10. Fill in the blanks in the following:

An isotope of an element has a valence of two positive, an atomic number of twenty, and an atomic weight of forty. The nucleus is equivalent to _____ protons and _____ neutrons. The first shell has _____ electrons, the second shell has _____ electrons, the third shell has _____ electrons, and the valence shell has _____ electrons.

Chapter 33

The Alkaline Earth Family

1. Introduction. Substances which we now know as oxides of metals were formerly known as *earths*. Among these earths were some which formed an alkali with water, and were like the alkali metals in some of their reactions. These were known as the *alkaline earths*, and for some time they were thought to be elements. In 1808, Davy electrolyzed the fused hydroxides of the alkaline earths and obtained four metals which he named *calcium*, *barium*, *strontium* and *magnesium*. The first three metals are known as the *alkaline earth metals* and they fit into the second group of the periodic table. In the same group are beryllium, radium, zinc, cadmium and mercury. Radium is similar to barium, and beryllium and magnesium are sufficiently like the alkaline earths to be included with them, but they are also similar to zinc, cadmium and mercury. The latter are not like the alkaline earths and form the other sub-group. They form the B family while calcium, strontium, barium and radium form the A family.

The alkaline earth metals are metallic in appearance and in their properties. Their freshly prepared surfaces have a bright lustre but a coating of the oxide forms rapidly in the air. They are good conductors of electricity. They are ductile and somewhat malleable, and they are harder than the alkali metals.

All the metals of this family have a positive valence of 2. Their activity increases with increasing atomic weight. Beryllium oxide does not react with water, magnesium oxide

acts only slowly, while the oxides of the heavier members of the family react with water to form hydroxides. The hydroxides show increasing solubility and basic strength with increasing atomic weight. All of the metals will burn when heated in the air, and they unite with nitrogen to form nitrides. They combine readily with many of the non-metals, such as the halogens and sulphur. Calcium, barium and magnesium are the familiar ones so we will make only a passing mention of strontium and beryllium (see sec. 9).

CALCIUM

2. Occurrence. Calcium is too active an element to be found in the free state but it occurs in many compounds. It is found as *limestone*, $CaCO_3$; *dolomite*, $MgCO_3.CaCO_3$; *gypsum*, $CaSO_4.2H_2O$; *fluorspar*, CaF_2 and *asbestos*, $CaMg_3(SiO_3)_4$. Calcium is found in certain plant materials, and calcium phosphate is the chief inorganic constituent of animal bones. Calcium compounds are found in sea water.

3. Production, properties and uses of calcium. Calcium is obtained by the electrolysis of the molten chloride. The anode is a graphite cup which holds the molten calcium chloride. The cathode is an iron rod dipping into the fused salt. As the calcium is deposited on the cathode, the rod is raised slowly, so that a rod of calcium is formed as the electrolysis proceeds. This cell is shown in Fig. 172.

Calcium received its name from the Latin *calx* for lime. It is a silvery-white crystalline metal which is a little harder than lead. Calcium will burn in air producing a mixture of the oxide and nitride. It unites directly with hydrogen to form a hydride, CaH_2. This compound is known as *hydrolyte*, and will react with water to produce hydrogen and calcium hydroxide.

$$\mathbf{CaH_2 + 2\ H_2O \longrightarrow Ca(OH)_2 + 2\ H_2}$$

This is a convenient though expensive way of obtaining hydrogen.

Because of its property of combining with water, calcium is sometimes used to dry organic liquids. It is a good reducing agent, and is used to obtain certain metals, such as cesium, chromium and thorium, from their compounds. Many alloys utilizing calcium have been developed in recent years.

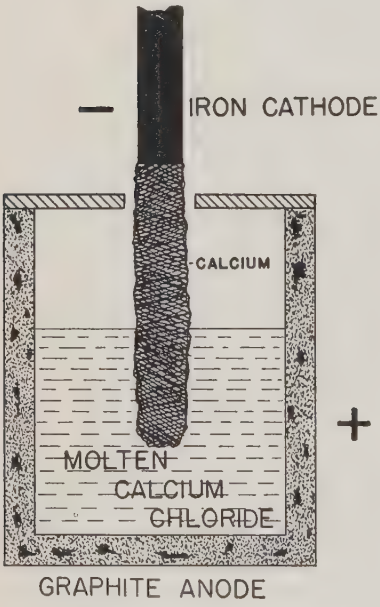


Fig. 172. The preparation of calcium by electrolysis.

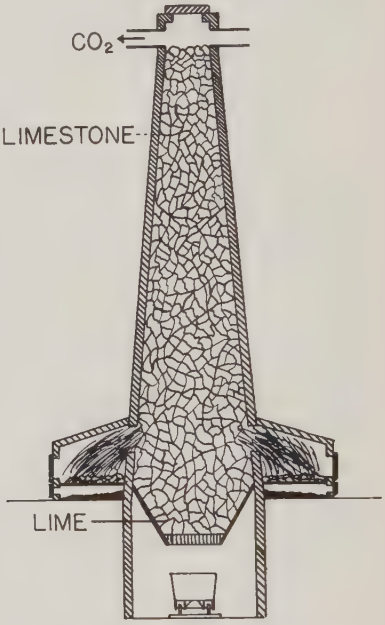


Fig. 173. Continuous production of lime in a vertical kiln.

4. Calcium oxide, CaO, commonly known as *quicklime*, melts at about 2570°C. When heated to a high temperature it emits a bright light known as *lime light*. Before the use of electricity lime light was used as a spot light in theatres. Calcium oxide is normally a white solid which may be slightly yellow in colour due to the presence of impurities. It is made by heating limestone in a kiln, which is a vertical

furnace about 60 feet in height and from 10 to 15 feet in diameter. The reaction is as follows:

$$CaCO_3 \rightleftarrows CaO + CO_2$$

This reaction is reversible, and the carbon dioxide must be removed rapidly to ensure complete decomposition of the limestone. The kiln is heated by coal or gas fires which open directly into it, and the draught produced removes the carbon dioxide, which may be collected if desired. This is the most common method of obtaining carbon dioxide for industrial purposes. The temperature used is about 1000°C. The use of too high a temperature causes impurities which are in the limestone to form silicates with the lime which prevent proper slaking of the quicklime. The lime kiln is shown in Fig. 173. You have already studied this process as a method of producing carbon dioxide.

Freshly prepared quicklime reacts violently with water to form *calcium hydroxide* or *slaked lime*. When quicklime is exposed to the air it will absorb both water and carbon dioxide, with the latter reforming calcium carbonate. This mixture is known as *air-slaked lime* and is of no value.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$
$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

Because of its ability to combine with water calcium oxide is often used as a drying agent for alcohol and ammonia. Mixed with solid sodium hydroxide it is known as *soda lime* and is used to remove water and carbon dioxide from gases.

Quicklime is used in the manufacture of hydrated lime, as a flux in the smelting of certain metals, in the manufacture of glass, and in the production of calcium carbide and calcium cyanamide.

5. Calcium hydroxide is a white powder which is slightly soluble in water. This substance is an exception to the general rule for the effect of temperature on the solubility of solids in liquids as its solubility decreases as the temperature increases. Its solution in water is known as *limewater*, and is a moderately strong base, which is used frequently because of its low cost. Because it is the cheapest basic substance, calcium hydroxide is used in the preparation of other alkalies, bleaching powder and insecticides. Any base softens animal tissues so calcium hydroxide is used for the removal of hair from hides in leather manufacture; in softening water because it converts calcium bicarbonate into insoluble calcium carbonate; and in the manufacture of paper, cement, plasters and other substances.

Mortar is made by mixing slaked lime with three or four times its weight of sand and making it into a paste with water. When used between stones or bricks the water evaporates and the residue hardens due to the absorption of carbon dioxide from the air and the formation of calcium carbonate.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

The crystals of calcium carbonate become interlaced and provide a porous structure which permits the entrance of carbon dioxide to the innermost parts. The gradual setting of mortar goes on for some time.

Plaster for interior walls was formerly composed of calcium hydroxide, sand and hair, with a finish coating of pure calcium hydroxide. The plaster in use today consists generally of plaster of Paris. Plaster used for exterior walls is known as *stucco*. It is composed of sand bound together with a mixture of lime and cement. Types of stucco have been in use for many thousands of years.

6. Calcium chloride, $CaCl_2$, is a white salt which is very soluble in water. It crystallizes from water as the hexahydrate, $CaCl_2.6H_2O$. When this hydrate is heated it loses water in steps and finally forms the monohydrate, $CaCl_2.H_2O$. When the monohydrate is heated to a high temperature the anhydrous salt, $CaCl_2$, is formed. The monohydrate is a porous deliquescent substance which is often used on roads and as a drying agent for gases and organic liquids.

Calcium chloride is usually obtained as a by-product of the Solvay process or other industries. Because of its unusually great solubility it is used as a brine in cold storage plants. A solution which does not freeze until $-55°C.$ can be obtained by dissolving the hexahydrate in water.

7. Calcium carbonate, $CaCO_3$, is the most abundant calcium compound found in nature. It occurs in two crystalline forms, *calcite* in the hexagonal and *aragonite* in the rhombic system. The most common form of calcium carbonate is *limestone* which occurs as stratified layers of rock which were formed by deposition on the bottom of ancient seas. These deposits have been covered by other material and have been elevated above their original position by geological changes taking place during many thousands of years. Limestone is not pure calcium carbonate, and may be of various colours because of impurities. Under the action of pressure and heat some deposits of limestone have been turned into *marble*, which is composed of small crystals of calcite. *Iceland spar* is practically pure calcite. *Chalk*, *marl* (a mixture of clay and calcium carbonate), *pearls*, *shells* and *coral* are other forms in which this well-known calcium compound may be found.

Large quantities of calcium carbonate are used in the preparation of quicklime, to neutralize acids in soil, in the manufacture of cement, glass and many other substances. Finely ground chalk, known as *whiting*, is used in preparing putty and pigments. *Precipitated chalk*, made by precipitating calcium carbonate from solutions, is used in some dental pastes and powders.

8. Calcium bicarbonate. Calcium carbonate is not very soluble in water, but if the water contains dissolved carbon dioxide it will dissolve more readily, as it is changed into the more soluble *calcium bicarbonate*.

$$\mathbf{CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2}$$

Rain-water contains some dissolved carbon dioxide, and surface waters dissolve the gas which is produced in the soil during the decay of organic materials. When this solution of carbon dioxide passes through limestone deposits, the rock will be dissolved, and caves may be formed. If water trickles through the roof of a limestone cave the carbon dioxide will evaporate from the water, and on the removal of the carbonic acid, calcium carbonate will be deposited. As this process goes on, a formation of calcium carbonate, called a *stalactite*, will project downward from the roof. If a similar process

Courtesy Philip Gendreau

Fig. 174. Calcium carbonate icicles called stalactites reach down to meet the stalagmites building up on the floor of this limestone cavern.

takes place when the water drips onto the floor, a formation called a *stalagmite* will be built up toward the roof (see Fig. 174). In some cases these formations will join together and form a pillar. If water containing calcium bicarbonate in solution is heated the bicarbonate will be converted into the carbonate, which will be deposited.

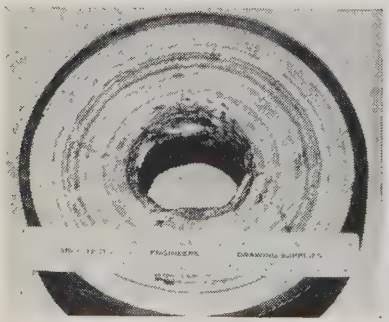
$$Ca(HCO_3)_2 \xrightarrow{\text{heat}} CaCO_3 + H_2O + CO_2$$

9. Calcium sulphate occurs in nature as *gypsum*, $CaSO_4.2H_2O$, and as the anhydrous form, *anhydrite*, $CaSO_4$. The hydrate is found in different crystalline forms as *alabaster*, *satin spar* and *selenite*. If gypsum is heated at a temperature of about 125°C. it will be partially dehydrated to form plaster of Paris $(2CaSO_4).H_2O$. When plaster of Paris is mixed with water, it forms a substance which has the same composition as gypsum, but which is more difficult to dehydrate. Plaster of Paris sets very rapidly, and expands slightly on setting, so it is used widely in surgical casts, models, statuary, etc., and in the manufacture of plaster for interior walls. Large quantities of gypsum are pulverized, dehydrated, and mixed with asbestos, sawdust, or similar material. The mixture is then wetted with water and moulded into blocks, boards, tiles etc. to be used as building material. Gypsum is the chief constituent of blackboard crayons.

10. Hard water. Waters which contain salts of calcium, magnesium and iron in solution are said to be *hard*. Almost all natural waters except rain-water are hard. If the water contains the bicarbonate of either calcium or magnesium, heating will drive out carbon dioxide and cause the formation and precipitation of the carbonate. This precipitate will form a crust in boilers and other vessels in which the water is heated. This crust acts as an insulator, so that more heat will be required. In addition, the iron which is protected

by the insulating crust may get red hot, which increases its liability to oxidize and become weak. Such a crust forming in a boiler is known as *boiler scale* (see Fig. 175).

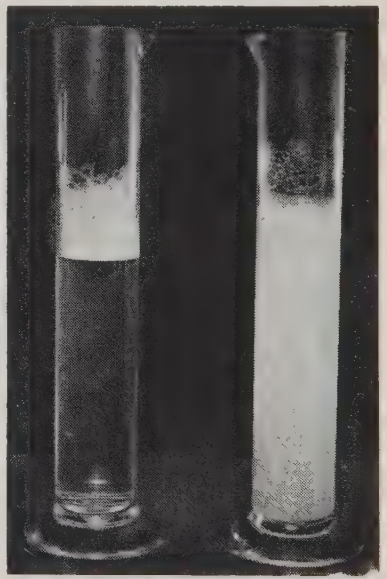
When hard water is used for washing, the soap will form a compound with the bicarbonates of calcium or magnesium and precipitate as a curd. This reaction uses a lot of soap, and thus the use of hard water for laundry purposes is wasteful. Many of the sulphonated oils are good wetting agents and they do not form insoluble salts with the metal ions in hard water. They form a lather in hard water and are known as the "soapless" soaps.



Courtesy Permutit Co.

Fig. 175

Fig. 175. Boiler scale in an iron pipe.



From Bayles & Mills: "Basic Chemistry", courtesy The Macmillan Company

Fig. 176

Fig. 176. Soap in soft and hard water.

Hardness produced by calcium or magnesium bicarbonates is known as *temporary hardness*, and may be removed by heating the water and filtering off the resulting precipitate. Temporary hardness is usually removed by adding slaked lime

in the exact amount required by an analysis of the water. The carbonate which is produced is filtered off.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\ CaCO_3 + 2\ H_2O$$

When water comes into contact with gypsum some calcium sulphate will dissolve. Hardness caused by calcium and magnesium sulphates, as well as by some other salts which cannot be precipitated by heating, is known as *permanent hardness*. To remove permanent hardness, substances which will convert the calcium and magnesium salts into compounds which will precipitate must be added to the water. This process is known as *water softening*.

11. Water softening. Various substances can be used to soften water. Sodium carbonate converts calcium and magnesium ions into the normal carbonate which may be removed by filtration. In the case of calcium sulphate, this may be represented by the following equation:

$$CaSO_4 + Na_2CO_3 \longrightarrow \underline{CaCO_3} + Na_2SO_4$$

A suspension of calcium hydroxide in water changes the bicarbonate into the carbonate, but does not affect any sulphate which may be present. It also changes soluble magnesium salts into the insoluble magnesium hydroxide. Its reaction with the bicarbonate is shown in sec. 10.

Naturally occurring sodium aluminum silicate, $NaAlSiO_4$, is known as *zeolite*. An artificial material of about the same composition is called *permutite*. If water containing calcium or magnesium ion is passed through a thick bed of this substance those ions are displaced by the sodium ion of the zeolite and the water is softened.

$$2\ NaAlSiO_4 + CaSO_4 \longrightarrow Na_2SO_4 + Ca(AlSiO_4)_2$$

After the permutite has been used for some time brine may be passed through it, when the process of displacement will be

reversed, the calcium of the permutite being displaced by sodium and the material restored to its original composition.

$$Ca(AlSiO_4)_2 + 2\ NaCl \longrightarrow CaCl_2 + 2\ NaAlSiO_4$$

The reversal of the reaction depends upon the concentration of the sodium ions. By the use of two sets of filters this process may be operated continuously, one filter softening the water while the other is being regenerated by brine. This process is used in homes and laundries and removes both temporary and permanent hardness in water.

Courtesy Aluminum Co. of Canada

Fig. 177. Rotary kilns are used for burning cement, limestone, gypsum, etc.

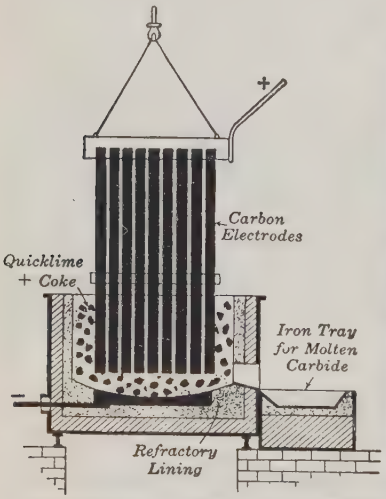
12. Cement. Cements are materials which will "set" to a solid after being mixed to a paste with water and allowed to stand. The most common cement is *Portland cement* which is so named because of its likeness to the stone found near the

town of Portland in England. The ancient Romans were familiar with the use of cement and some of their ruins show the use of cements which were not much different in composition from those in use today. Portland cement is made from a mixture of limestone and clay. The materials are finely ground and well mixed, then placed in a rotary kiln. This kiln is a long rotating tube which is inclined slightly (see Fig. 177). The charge of limestone and clay is fed into the upper end while the lower end is heated to a temperature of about 1500°C. The materials of the charge become partially fused and form a mass of small lumps called *clinker* which is composed of the silicates and aluminates of calcium, iron and magnesium. This clinker falls out of the lower end of the kiln and after cooling is ground to a fine powder called cement. When water is added to the cement stable solid hydrates and gels are produced. A small amount of gypsum is mixed with the cement during grinding to retard the time of setting, otherwise the cement might set before it could be placed in position. Since such a cement sets under water it is often called hydraulic cement. The manufacture of cement requires a large expenditure of power because of the fine grinding but it is still a reasonably priced structural material. When a mixture of crushed rock, sand, water and cement is allowed to stand, an artificial stone called *concrete* is produced. For structural use, concrete may be reinforced by burying iron rods or beams in the forms before the concrete is poured.

13. Calcium carbide, CaC_2, is an important compound prepared by heating a mixture of calcium oxide and coke up to 3000°C. in an electric furnace fitted with carbon electrodes. The process was invented by a Canadian, Thomas L. Willson. Lime reacts with the carbon, forming carbon monoxide and calcium carbide.

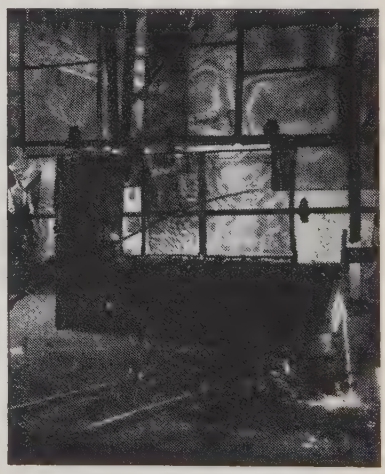
$$CaO + 3\ C \rightleftarrows CaC_2 + CO$$

Pure calcium carbide is crystalline and transparent but the commercial product is in the form of soft grey porous lumps. Because of the large amount of energy required calcium carbide is manufactured where cheap electricity is available, such as at Niagara Falls, Ontario, and Shawinigan Falls, Quebec. Limestone is converted to lime by heating in a rotary kiln and three parts of lime together with two parts of coke are placed in an iron box lined with fire-brick. A layer of graphite blocks on the bottom makes one electrode and the other electrode is made of several half-ton graphite blocks in the charge. A vast quantity of electricity flows from lump to lump of coke making hundreds of huge electric arc lamps which heat the charge to the melting point of calcium carbide. The carbide flows away as it is formed and the carbon monoxide burns at the top of the furnace. It must be allowed to escape freely as the reaction is reversible. The carbide is chilled and loaded into railway cars or other conveyors.



From Black & Conant: "New Practical Chemistry", courtesy The Macmillan Company

Fig. 178. Diagram of a carbide furnace.



Courtesy Shawinigan Chemicals Ltd.

Fig. 179. Tapping a carbide furnace.

Calcium carbide reacts with water to form calcium hydroxide and acetylene.

$$CaC_2 + 2\ H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

It was developed for lighting purposes in homes, streets, automobiles and bicycles but electricity has completely displaced it.

Organic chemists have learned how to convert it to acetic acid and a number of other important chemicals so a great synthetic chemical industry based on calcium carbide has developed at Shawinigan Falls, Quebec.

14. Calcium cyanamide. Calcium carbide reacts with nitrogen at 1000°C. to form calcium cyanamide.

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

Pure nitrogen is made by the liquefaction of air and passed into the carbide in an electrically heated oven. The commercial cyanamide is dark grey due to the free carbon and was once widely used as a fertilizer. It added lime to the soil and its nitrogen was eventually converted into nitrates by the soil bacteria. Its use as a fertilizer has declined but it can be used to make plastics. During the last war guanidine, which is related to urea, was made from cyanamide and nitrated with nitric and sulphuric acid to make an important explosive. Canada is a leading producer of these chemicals from cyanamide with plants at Niagara Falls and Shawinigan Falls.

BARIUM

15. Preparation and properties of barium. Barium may be prepared in a similar manner to calcium by the electrolysis of the molten chloride. It is a silvery white metal which unites readily with oxygen, even spontaneously in moist air.

It is about as soft as lead. The name signifies "heavy" and is derived from the name of the oxide *baryta*. The most important minerals containing barium are *heavy spar*, or *barytes*, $BaSO_4$; and *witherite*, $BaCO_3$. An alloy of barium and nickel is used to make points for spark plugs. Another important alloy is *Frary metal*, which contains barium, calcium and lead.

16. The oxides of barium. *Barium monoxide*, BaO, may be prepared by the decomposition of barium carbonate but a higher temperature is required than in the case of the decomposition of calcium carbonate. The oxide is usually prepared by heating the carbonate with powdered charcoal.

$$\mathbf{BaCO_3 + C \longrightarrow BaO + 2\ CO}$$

The oxide unites with water to form the hydroxide.

$$\mathbf{BaO + H_2O \longrightarrow Ba(OH)_2}$$

Barium peroxide, BaO_2, is produced by heating the monoxide in a stream of oxygen or air at a temperature of about 550°C. At a higher temperature of about 750°C. the action is reversed and oxygen is liberated. This reaction was used as a method of preparing oxygen and is known as *Brin's process*. When barium peroxide is treated with sulphuric acid, hydrogen peroxide is obtained (see Chap. 6, sec. 9).

17. Barium hydroxide is the most soluble of the hydroxides of this family and therefore gives the greatest concentration of hydroxyl ion. The solution in water is known as *baryta water* which is used in the laboratory for making alkaline standards. Solutions of barium hydroxide will absorb carbon dioxide from the air, but the carbonate which is formed will be precipitated and will not remain in solution.

18. Barium sulphate, $BaSO_4$, is the most abundant mineral in which barium occurs and is used frequently as a

source of barium compounds. The sulphate is changed into the sulphide by reducing it with carbon.

$$BaSO_4 + 4\ C \longrightarrow 4\ CO + BaS$$

Then it will dissolve in solutions of hydrochloric or nitric acid to form other salts. If the sulphate is fused with sodium carbonate, barium carbonate will be obtained.

$$BaSO_4 + Na_2CO_3 \longrightarrow BaCO_3 + Na_2SO_4$$

Barium sulphide reacts with zinc sulphate to form zinc sulphide and barium sulphate. The mixture of the two slightly soluble salts, known as *lithopone*, is used in paint. Lithopone has some advantages over white lead as it does not turn black when exposed to hydrogen sulphide and it is not poisonous.

$$BaS + ZnSO_4 \longrightarrow BaSO_4 + ZnS$$

Barium sulphate is used in white paint, where it is known as *permanent white*. It is also used as a filler in the manufacture of paper, rubber, linoleum and oilcloth. Since it is quite insoluble in water it is used in quantitative analysis in the determination of either barium or sulphate ions. Barium sulphate is used in taking photographs of the intestinal tract since it is opaque to X-rays, and in oil-well drilling because of its great density. Barium chloride is a familiar laboratory reagent and both it and the nitrate are used to produce a green light in fireworks.

STRONTIUM

19. Properties and uses of strontium. Strontium is named after *Strontian*, a village in Scotland, where the mineral *strontianite*, $SrCO_3$, was first found. The metal may be produced in the same manner as calcium but the production is more difficult. It has no commercial uses. The

compounds of strontium are similar to those of calcium. The hydroxide is a moderately strong base and is sometimes used in sugar refineries to separate cane sugar from molasses. Strontium hydroxide forms an insoluble compound with sucrose (cane sugar) which enables it to be separated from some of the other sugars which are present.

MAGNESIUM

20. Occurrence, preparation and uses of magnesium. Magnesium occurs as *dolomite*, $CaCO_3.MgCO_3$; *magnesite*, $MgCO_3$; and in several silicates as *meerschaum*, *asbestos*, *talc*, *soapstone* and *olivine*. Magnesium metal can be obtained like aluminum by the electrolysis of a mixture of magnesium oxide dissolved in magnesium fluoride and the fluorides of sodium and barium, but is more easily prepared by the electrolysis

Courtesy Dow Chemical Company

Fig. 180. Furnaces used for electrolytic magnesium production.

of magnesium chloride. The magnesium chloride is usually obtained from sea-water by fractional crystallization. The chloride is fused with the chlorides of sodium, potassium or calcium, and the mixture then electrolyzed. It can be prepared from dolomite by a process developed in Canada by Dr. L. M. Pidgeon involving reduction with ferrosilicon and distillation in a vacuum furnace.

Magnesium is a silvery white metal with a specific gravity of 1.7, which makes it useful in the preparation of very light alloys of aluminum. It does not react with oxygen at ordinary temperatures, since it is protected by the formation of a film of the oxide, but it burns at higher temperatures with a dazzling white light. For this reason it is used in photographic flash powder. It was first made in Canada for this purpose during World War I.

21. Magnesium oxide and hydroxide. *Magnesium oxide*, MgO, or *magnesia*, may be prepared by burning the metal or by heating the carbonate. It is a white powder similar to calcium oxide. It reacts with water to form the hydroxide but more slowly than does calcium oxide. It has a very high melting point and is frequently used in making fire-brick and linings for furnaces, also in making Sorel cements and for various building materials.

Magnesium hydroxide, $Mg(OH)_2$, is less basic and less soluble in water than calcium hydroxide. It may be precipitated from solution by a soluble hydroxide, other than ammonium hydroxide. It will not precipitate in the presence of ammonium ion, since that ion causes the formation of ammonium hydroxide which is so slightly ionized that there are not sufficient hydroxyl ions remaining to form magnesium hydroxide.

22. Other magnesium compounds. *Magnesium carbonate*, $MgCO_3$, is slightly soluble but the bicarbonate, $Mg(HCO_3)_2$, is more soluble. If sodium carbonate is added very slowly

to a solution of a magnesium salt, the basic carbonate, $Mg(OH)_2.3MgCO_3.3H_2O$, *magnesia alba* or *milk of magnesia*, is formed. This compound is used in polishing pastes, dental powders and insulating materials.

Magnesium chloride, $MgCl_2$, occurs as a double salt *carnalite*, $MgCl_2.KCl.6H_2O$, in the Stassfurt deposits, from which the salt may be obtained. It crystallizes from water as the hexahydrate. Magnesium chloride is present in sea-water, and is found as an impurity in table salt, where it is very objectionable owing to its deliquescence. The moisture picked up from the air causes the salt to cake and not run freely from shakers. Magnesium chloride causes objectionable hardness in water, as the salt is partially hydrolyzed and hydrochloric acid is formed. The acid corrodes boilers and may prove dangerous.

$$\mathbf{MgCl_2 + H_2O \longrightarrow 2\ HCl + MgO}$$

For this reason, sea-water cannot be used in steam boilers.

Magnesium sulphate is found as *kieserite*, $MgSO_4.H_2O$, and *epsomite*, $MgSO_4.7H_2O$. It is found also in mineral waters and in the sea. It is used in medicine as *Epsom Salts*, in weighting cotton and in sizing paper.

BERYLLIUM

23. Properties and uses of beryllium. The metal beryllium was isolated by Wöhler in 1828 by the action of potassium on beryllium chloride. It is found in nature in the *beryls* which are beryllium aluminum silicates. Among the beryls are the gems, *emerald*, which is green, and *aqua marine*, which is a pale blue. Various compounds of beryllium are known but they are not of importance.

Beryllium is much less metallic than the other alkaline earths and this follows from the general trend that non-metallic properties increase with the number of the group and with a decrease in atomic weight.

RADIUM

24. Radium. Gold is dirt-cheap compared to radium which is so scarce that it costs about 30,000 times as much.

We have already told you how radium was discovered in the search for the source of the invisible rays which came from certain minerals and how the study of these rays led men to a new conception of the nature of matter (see Chap. 31). Radium has two sets of properties. On the one hand it is an alkaline earth metal, has a valence of 2, acts energetically on water to displace hydrogen, produces a strong base and in general forms the same type of compounds as barium;

TABLE 32—SOME PROPERTIES OF THE ALKALINE EARTHS

Property	*Beryllium*	*Magnesium*	*Calcium*	*Strontium*	*Barium*	*Radium*
Atomic Weight	9.02	24.32	40.08	87.63	137.36	226.05
Melting Point	1350	651	810	752	850	960
Valence	2	2	2	2	2	2
Action on Water	None	Very slow	Slow	Fast	Rapid	Vigorous
Strength of Base	Insoluble	Weak	Strong	Strong	Strong	Strong
Solubility of Base	Insoluble	0.0016	0.185	0.41	5.6	.....
Chloride Melts	440	708	772	873	962	.....
Solubility of Sulphates	42.5	26.0	0.298	.0113	.00023	.....
Colours Flame	No	No	Brick red	Crimson	Light green	Carmine

on the other hand it disintegrates spontaneously into a series of new elements. These qualities make it at once the most fascinating natural element in the world (see Chap. 37, sec. 2).

25. Summary of periodic properties. The alkaline earth family is said usually to include beryllium and mag-

nesium along with calcium, strontium, barium and radium. Beryllium and magnesium belong to the two short periods of the periodic table and their properties are slightly different from those of the other members of the family. They are far less metallic, their hydroxides are little soluble and their chlorides are hydrolyzed by water because of the weakness of the bases. Beryllium is less like the alkaline earths than magnesium. Table 32 will illustrate the similarities and differences.

Question Summary

1. How did the family of alkaline earths get its name?
2. Where is calcium found in nature?
3. (*a*) How is calcium obtained?
   (*b*) What compound of calcium provides an easy way of getting hydrogen?
4. (*a*) How is calcium oxide prepared?
   (*b*) What are some of the uses of calcium oxide?
5. (*a*) How is calcium hydroxide prepared?
   (*b*) Of what is mortar composed?
   (*c*) Of what is plaster made?
6. How is calcium chloride obtained?
7. (*a*) In what forms is calcium carbonate found in nature?
   (*b*) What are the uses of calcium carbonate?
8. What part does calcium bicarbonate play in nature?
9. (*a*) How does calcium sulphate occur in nature?
   (*b*) What are the uses of calcium sulphate?
10. Discuss the formation of hard water.
11. Discuss the various methods of softening water.
12. How is Portland cement prepared?
13. (*a*) How is calcium carbide prepared?
    (*b*) How is acetylene prepared? What are its uses?
14. (*a*) How is calcium cyanamide prepared?
    (*b*) Describe the cyanamide process of fixing nitrogen.
15. How may barium be obtained?
16. Describe Brin's process.

17. Why is barium hydroxide used to make standard basic solutions?

18. (*a*) What properties of barium sulphate make it useful?
(*b*) What is lithopone and what are its uses?
(*c*) How are barium compounds used in X-ray work?

19. (*a*) Discuss the metal strontium and its compounds.
(*b*) What is the chief use of strontium hydroxide?

20. (*a*) How is magnesium prepared and what are its uses?
(*b*) Why did Canada embark upon a programme of magnesium production?

21. (*a*) Why does not magnesium hydroxide precipitate in ammonium solutions?
(*b*) What is magnesia used for?

22. (*a*) Name some magnesium compounds and their uses.
(*b*) Why cannot sea-water be used in boilers?

23. (*a*) How does the periodic table account for the properties of beryllium?
(*b*) Discuss the metal beryllium and its uses.

24. (*a*) Give some reasons why radium is such an unusual metal.
(*b*) Give some reasons for putting radium in the alkaline earth family.

25. In what ways does Table 32 bring out the periodic behaviour of the alkaline earth metals?

Chapter **34**

The Boron and Aluminum Group

1. Introduction. Group III of the periodic table contains at least twenty-three elements. Two of these elements, *boron* and *aluminum*, are well known but the others are quite rare. Boron is a non-metal. Aluminum, the most important member of the group, is amphoteric, though definitely a metal. The remaining elements are all metals. It is now believed that the radioactive actinide series belongs to this group.

BORON

2. Occurrence. Boron is not abundant and constitutes only a small portion of the earth's crust. It occurs as *boric acid*, H_3BO_3, in hot springs near Tuscany in Italy, and the crude acid which crystallizes from the water is known as *Tuscany acid*. It is found in several borate minerals and is also present in small quantities in sea-water, in some oils and in the ashes of certain plants.

3. Preparation. Amorphous boron may be prepared by reducing the oxide with an active metal, such as potassium, sodium, magnesium or aluminum. Boron may also be obtained from boron tribromide by the action of hydrogen at the very high temperature of a heated filament.

4. Properties. Amorphous boron melts at about 2000°C. and solidifies to form a hard brittle solid. Boron burns with a green flame and oxidizes slowly at lower temperatures. It unites with nitrogen, hydrogen, sulphur and the halogens. With carbon and silicon it forms extremely hard crystalline substances similar to diamond. When heated with certain

metals it forms borides. It does not dissolve in acids but nitric acid oxidizes it to boric acid. It dissolves in molten alkalis to form borates. In general boron acts like a non-metallic element with a valence of 3.

5. Boric acid. *Orthoboric acid*, H_3BO_3, commonly known as *boric* or *boracic acid*, may be obtained from hot springs by evaporation of the water. It is usually prepared by heating a solution of borax with sulphuric acid.

$$Na_2B_4O_7 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2B_4O_7$$
$$5\ H_2O + H_2B_4O_7 \longrightarrow 4\ H_3BO_3$$

Boric acid is not very soluble and it precipitates as thin pearly flakes which are slippery to the touch. It is a mild antiseptic and is frequently used as an eye wash and a preservative. It is also used in making glaze for some kinds of pottery. It is a weak acid, its salts are unstable and only a few of them are known. One of the best known is magnesium orthoborate, $Mg_3(BO_3)_2$.

6. Borax. When orthoboric acid is neutralized by sodium hydroxide the salt obtained is sodium tetraborate. At temperatures below 62°C. this salt crystallizes from solution as the decahydrate, $Na_2B_4O_7.10H_2O$, which is known as *borax*.

When heated, borax melts, loses water and swells up into a white porous mass as the water is driven off. The mass finally melts to a clear glass, known as *borax glass*, which is anhydrous borax. This glass will dissolve many metallic oxides which will impart a characteristic colour to the glass. The colours produced by the action of different metallic oxides on borax beads in oxidizing and reducing flames are given in Table 33, page 504.

The solution of metallic oxides in borax is supposed to be due to an excess of boric oxide. Borax may be expressed as $2NaBO_2.B_2O_3$. The metallic oxide unites with the boric oxide. In the case of copper the reaction would be

$$Na_2B_4O_7 + CuO \longrightarrow Cu(BO_2)_2 + 2\ NaBO_2$$

TABLE 33—COLOURS OF BORAX BEADS PRODUCED BY SOME METALLIC OXIDES

Oxide	*Oxidizing flame*	*Reducing flame*
Copper	Green (hot); Blue (cold)	Colourless or red
Cobalt	Blue	Blue
Chromium	Green	Green
Iron	Brown (hot); Yellow (cold)	Olive
Nickel	Violet (hot); Yellow-brown (cold)	Grey, opaque
Manganese	Purple	Grey, opaque

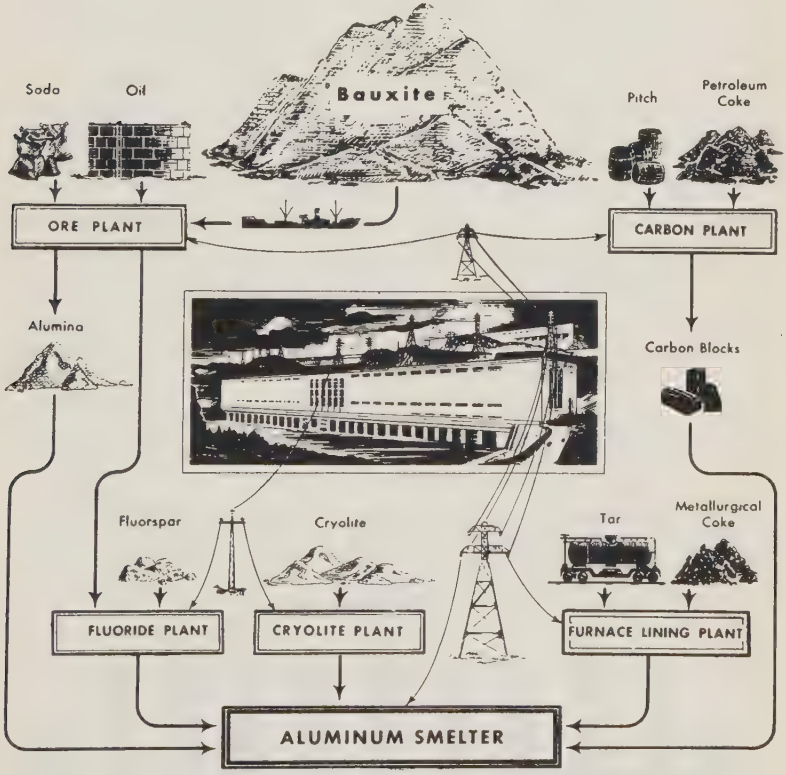
Borax is used in the manufacture of glass, enamels and glazes. Its use in glass is to increase the coefficient of refraction, to lower the coefficient of thermal expansion and to decrease crystallization. Because it hydrolyzes to give an alkaline solution it is used in water softening, in soaps, as an alkali, as a food preservative, as a mordant, in cleaning hides and silk and to produce a gloss on paper. It is also used as a flux in soldering as it will dissolve the film of oxide from the metals, making the surfaces clean.

ALUMINUM

7. Occurrence. The alchemists gave the name *alum* to any substance which had an astringent taste; and long before the metal was prepared aluminum oxide was recognized as the base of alum. The name of the element is derived from the word "alum".

Aluminum is the third most abundant element in the earth's crust and it is the most abundant metal. Clay, slate and shale contain large amounts of aluminum, but they are not used as a source of the metal since they are difficult to reduce. The most important ore of aluminum is *bauxite*, which is a mixture of hydrated aluminum oxide, $Al_2O_3.2H_2O$ and iron oxide, Fe_2O_3. Another compound, *cryolite*, Na_3AlF_6, is used in the

production of the metal. Aluminum is also found in *corundum*, Al_2O_3; *emery*, a mixture of Al_2O_3 and Fe_3O_4; *garnet*, a mixed silicate of aluminum, calcium, magnesium and iron; and *turquoise*, which contains basic aluminum phosphate. The oxide, Al_2O_3, together with small amounts of other metallic oxides, forms the gems *ruby*, *sapphire* and *topaz*.



Courtesy Aluminum Co. of Canada

Fig. 181. It takes about seven tons of raw materials to make a ton of aluminum.

8. Metallurgy. Aluminum was prepared by Oersted in 1825 by the reduction of aluminum chloride with metallic potassium. This process was very expensive and the element was obtained as a light grey powder. It was prepared in

some quantity from bauxite by Deville in 1854, but was so expensive that it was only a curiosity at about fifteen dollars a pound.

While a student in college, Charles Martin Hall became interested in the problem of the production of aluminum and in 1886 succeeded in obtaining it by the electrolysis of a solution of bauxite in molten cryolite. Aluminum was also prepared by the same method in France by Paul Heroult. It is interesting to note that Hall and Heroult were each born in the same year, 1863; made their famous discovery in the same year, 1886; and died in the same year, 1914. Although the production of aluminum by the electrolytic method requires a large amount of electrical energy, and the preliminary purification of the bauxite is expensive, the metal now sells for about fifteen cents a pound (see Fig. 181).

In the Hall process the electrolysis is carried out in an iron tank which is lined with a compressed mixture of coke and tar. This mixture is applied to the tank and then baked, so that the tank is coated with a layer of carbon which serves as the cathode of the cell. The anodes are carbon rods which are arranged so that they may be lowered into the tank. This

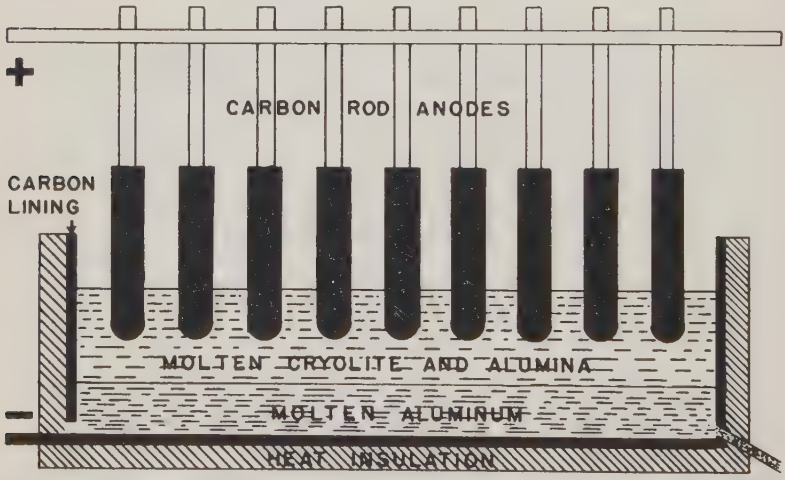


Fig. 182. Diagram of furnaces used for the electrolytic production of aluminum.

cell is shown in Fig. 182. At the start of the process the anodes are lowered until they touch the bottom and then raised so that an arc is formed. When the arc is formed cryolite is poured in and is melted by the heat of the arc.

When the cryolite is melted the bauxite is poured in and dissolves in the melted cryolite. The anodes are then raised and the electrolysis commences. The temperature of the molten cryolite is greater than the melting point of aluminum, so that the metal which is liberated at the cathode remains in the molten state and may be drawn off from time to time. The liberated oxides may be collected at the anodes and fresh bauxite added as it is required. The bauxite must be as pure as possible. Commercial bauxite is pulverized and heated with sodium hydroxide to form sodium aluminate, which is then hydrolyzed to form the pure oxide.

Aluminum may be purified by the *Hoope's process.* An alloy of commercial aluminum and copper is prepared and used on the bottom of a cell as the anode. The electrolyte consists of a fused mixture of fluorides of aluminum, barium and sodium in which aluminum oxide is dissolved, and the cathode consists of a top layer of pure aluminum. Large quantities of aluminum are prepared in Canada at Arvida, Quebec.

9. Properties of aluminum. Aluminum is a silvery-white metal. It is malleable and ductile at ordinary temperatures but becomes brittle when heated to more than 150°C. It has a higher tensile strength than most of the metals, except iron and copper, and is a good conductor of heat and electricity. Aluminum is difficult to machine as it sticks to the tools; neither does it make very good castings. These difficulties may be overcome by alloying small amounts of other metals with the aluminum.

Aluminum reacts slowly with the oxygen of the air until a film of oxide is produced and forms a protective coating. If the metal is in the form of a very fine powder, or is heated to a high temperature, it will burn with a brilliant flame. Because of the deposition of oxide on the surface it does not react with water, but it will displace hydrogen from strong acids such as hydrochloric acid.

$$2\ Al + 6\ HCl \longrightarrow 2\ AlCl_3 + 3\ H_2$$

It does not react at all with nitric acid because HNO_3 increases the oxide coating. It will dissolve in concentrated solutions of bases such as sodium or potassium hydroxide, giving off hydrogen and forming *aluminates*, because the oxide coating is amphoteric and the base removes it.

$$2\ Al + 2\ NaOH + 2\ H_2O \longrightarrow 2\ NaAlO_2 + 3\ H_2$$

The metal will combine directly with nitrogen, carbon, sulphur and the halogens.

10. Uses of aluminum. Aluminum may be used where a metal of great tensile strength, durability and low density is needed. It is used in the construction of aircraft, railway cars and trams or wherever lightness and strength is an important factor. Large quantities are used in the manufacture of kitchen utensils because it does not tarnish black. Aluminum foil is used as a wrapping for food and other products and in electrical condensers. An interesting use of aluminum foil is as an insulator. Although the metal is a good conductor of heat the shining surface reflects so much heat that the foil acts as a good insulator. Aluminum is not as good a conductor of electricity as is copper in wires of the same diameter, but it is a much better conductor than a copper wire of the same weight. Its use for transmission lines means that a wire may be used that is lighter in weight though greater in diameter, resulting in less strain on the supporting towers. Clean aluminum combines so readily with oxygen that it is used to remove oxygen from iron and steel and to prevent blow-holes in castings. Powdered aluminum is used in the thermite process and in the manufacture of metallic paint.

Aluminum forms several important alloys with various metals. *Magnalium* is a very important alloy of aluminum and magnesium; *duralumin* contains aluminum and copper together with small amounts of magnesium and manganese.

These alloys have a greater tensile strength than aluminum itself although they are very light. Some of the alloys with aluminum can be cast and machined.

11. Thermite. Aluminum has such a great affinity for oxygen that it will displace from their oxides the metals below it in the electrochemical series. This is the basis of the *Goldschmidt process* for making pure specimens of metals like chromium and manganese, and for welding by means of *thermite*. Thermite is a mixture of ferric oxide and finely powdered aluminum. If it is placed in a crucible and ignited by a piece of burning magnesium ribbon a violent reaction takes place and aluminum oxide and iron are produced.

$$Fe_2O_3 + 2\ Al \longrightarrow Al_2O_3 + 2\ Fe$$

The temperature of the reaction is about 3000°C. which is above the melting point of iron (1500°C.) and aluminum oxide (2050°C.), so molten iron collects at the bottom and molten aluminum oxide floats on the top. Thermite was once widely used for welding. In the welding of tram rails the two ends of rail which were to be joined were surrounded by a clay mould and preheated with blow-torches. A crucible containing the thermite was placed over the mould and the thermite ignited. The molten iron produced by the reaction was allowed to flow through a hole in the bottom of the crucible into the heated mould where it welded the rails together. This method of welding is still used for large castings like propellor shafts and rudders, where it is difficult to remove the broken pieces. The reaction occurred in the deadly fire bombs used in World War II.

12. The oxide of aluminum. *Aluminum oxide*, Al_2O_3, occurs in nature as *corundum* and the impure variety, *emery*. These substances are next to the diamond in hardness and are used as abrasives. By heating the precipitated hydroxide or bauxite in an electric furnace until a portion of the charge is fused, an artificial aluminum oxide is produced. This artificial compound is known as *alundum* and is used as an abrasive or in the manufacture of fire-brick. *Ruby*, containing oxides of iron and titanium; and *sapphire*, containing oxides of cobalt and chromium, are forms of aluminum oxide that are used as gems. By fusing the powdered oxides, artificial rubies and sapphires may be made. They have the same composition and appearance as the natural stones and can be distinguished from them only by the shape of the microscopic bubbles that appear in the stones.

13. Aluminum hydroxide, $Al(OH)_3$, may be prepared as a gelatinous precipitate by adding a small amount of a soluble hydroxide to a solution of an aluminum salt.

$$AlCl_3 + 3\ NaOH \longrightarrow \underline{Al(OH)_3} + 3\ NaCl$$

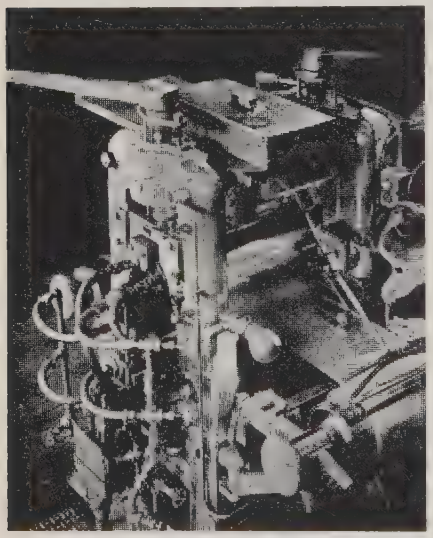
The hydroxide is amphoteric and may be dissolved by an excess of the base. In this case the hydroxide acts as an acid.

$$H_3AlO_3 + NaOH \longrightarrow NaAlO_2 + 2\ H_2O$$

The salt produced by this reaction is an *aluminate*. The hydroxide also acts as a base with acids to form aluminum salts.

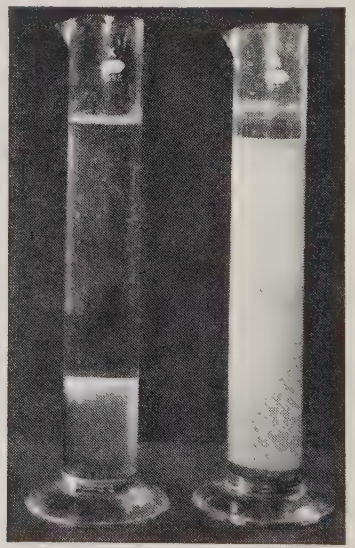
$$Al(OH)_3 + 3\ HCl \longrightarrow AlCl_3 + 3\ H_2O$$

Salts that are produced by the action of aluminum hydroxide and weak acids, such as carbonic, acetic and hydro-



Courtesy Aluminum Co. of Canada

Fig. 183.



From Bayles & Mills: "Basic Chemistry", courtesy The Macmillan Company

Fig. 184.

Fig. 183. Rolling of aluminum foil.

Fig. 184. Aluminum hydroxide precipitated in the first tube has carried down the suspended matter.

sulphuric acids, are hydrolyzed so strongly that some of them can be obtained only in the dry state. When dissolved in water they form a precipitate of aluminum hydroxide. This precipitate has important industrial applications. If cloth is soaked in a solution of aluminum acetate and then boiled, the resulting hydrolysis will cause the aluminum hydroxide to be precipitated between the threads and the cloth will be waterproof. Since aluminum hydroxide adsorbs many dyes it may be used as a mordant in dyeing, where it binds the dye to the textile material. Paper may be sized in this manner so that it will not absorb ink like blotting-paper does. Aluminum hydroxide may be used to purify water, since the precipitate will absorb or entrap many impurities and may be removed by filtration.

14. Compounds of aluminum. *Aluminum chloride*, $AlCl_3$, may be prepared by the action of chlorine upon aluminum or bauxite, in which case the anhydrous salt may be obtained. The anhydrous chloride may be purified by sublimation. It combines with water readily and is used as a reagent and a catalyst. A solution of the salt is obtained when hydrochloric acid acts upon aluminum hydroxide or the metal itself. Evaporation of the solution yields hexahydrate crystals, $AlCl_3.6H_2O$, but complete evaporation does not give the anhydrous salt, since it hydrolyzes, forming hydrochloric acid and the oxide.

$$2\ AlCl_3 + 3\ H_2O \longrightarrow 6\ HCl + Al_2O_3$$

The other halides resemble the chloride. They all form compounds with ammonia as $AlCl_3.6NH_3$, and the fluoride forms complex salts, of which cryolite, Na_3AlF_6, is an example.

Aluminum sulphate, $Al_2(SO_4)_3$, may be prepared by treating bauxite or clay with sulphuric acid. The salt crystallizes from solution as the hydrate, $Al_2(SO_4)_3.18H_2O$. While the early use of the term *alum* referred to any astringent substance

the word is now used to denote the double salts obtained by crystallizing two sulphates which have been mixed in equi-molecular proportions. Common alum is *potassium aluminum sulphate*, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, which may be prepared by dissolving equi-molecular proportions of potassium and aluminum sulphates in water and allowing the solution to crystallize. All alums form crystals in the same system and are known as double salts. They are hydrates containing 24 molecules of water. They are distinguished from complex compounds in that they form simple and not complex ions where the metal is a part of the negative ion. Common alum forms the ions, K^+, Al^{+++}, and SO_4^{--}. Other common alums are *ammonium alum*, *chrome alum* and *iron alum*. Aluminum sulphate and alum form gelatinous masses in water and are used in fire extinguishers, water purification, dyeing, paper sizing, and in photographic fixing solutions as a hardener for the gelatin. These uses depend, for the most part, on the hydrolysis of the aluminum salt and the production of aluminum hydroxide.

Mordants are insoluble gels which form in a fabric and serve to hold the dye to the textile, especially in the case of linen and cotton. The mordant adsorbs the dye and holds it fast to a fibre to which it would not attach itself. Salts which hydrolyze to give insoluble hydroxides are mordants.

A solution of aluminum sulphate which hydrolyzes and acts as an acid is used with sodium bicarbonate in the foam type of fire extinguishers to give a foam of carbon dioxide in a gelatinous mass of aluminum hydroxide. An extract of licorice or some other protective colloid is used to strengthen the foam and prevent the loss of carbon dioxide. A blanket of foam several inches thick can be formed quickly, effectively cutting off the supply of oxygen and extinguishing the fire. Such extinguishers are widely used in oil refineries, paint

factories, garages and other establishments using volatile inflammable solvents (see Fig. 69 in Chap. 13, sec. 16).

Aluminum silicates. Many of the silicate rocks contain aluminum in the form of complex silicates. Due to the thawing and freezing of water in the rocks, and the action of carbon dioxide and water as reagents, the rocks disintegrate. The aluminum silicates are often found in almost pure deposits. One of them is pure white and is known as *kaolin* (see Chap. 35, sec. 7).

15. Gallium. When Mendeléeff constructed his periodic table there was a gap in Group III. This he predicted would be filled by an element to which he gave the name of *eka-aluminum.* He also deduced the properties of this undiscovered element, and when Lecoq de Boisbaudrau found a new element in 1875 while studying some zinc ores, he found that its properties suited almost exactly the predictions made for eka-aluminum. The new element was named *Gallium* in honour of France. It is used in high-temperature thermometers because of its low melting point and high boiling point. See Table 25 in Chap. 30, sec. 5.

Question Summary

1. Name the two best-known elements of Group III and place them among metals and non-metals.

2. Where does boron occur on the earth?

3. (*a*) How may amorphous boron be prepared?
(*b*) How may crystalline boron be prepared?

4. What are the properties of boron?

5. What are the properties and uses of boric acid?

6. (*a*) How may borax be prepared?
(*b*) How are coloured borax beads produced?
(*c*) What are some of the uses of borax?

7. Where does aluminum occur on the earth?

8. (*a*) Give a brief account of the discovery of aluminum.
(*b*) How is aluminum prepared from its ores?
(*c*) How are the bauxite and the aluminum purified?

9. (*a*) What are the physical properties of aluminum?
(*b*) What are the chemical properties of aluminum?

10. (*a*) What are the advantages of using aluminum in electrical transmission lines as compared with copper?
(*b*) Give some other uses for aluminum.

11. (*a*) Describe the Goldschmidt process for making pure metals.
(*b*) Describe the industrial use of thermite.

12. Describe the various forms of aluminum oxide.

13. (*a*) What is the chemical behaviour of aluminum hydroxide?
(*b*) Give some industrial uses for aluminum hydroxide.

14. (*a*) Give some of the properties and uses of the aluminum halides, sulphates, and silicates.

(*b*) What is an alum? Name some of the common alums, and indicate their use in industry.

(*c*) How can a foam type fire extinguisher be made and where should it be used?

Chapter 35

The Silicon-Tin-Lead Family

1. Introduction. Group IV of the periodic table consists of two sub-groups: the A family contains the non-metals carbon and silicon, and the metals germanium, tin and lead; the B family contains the four elements, titanium, zirconium, hafnium and thorium. The first sub-group contains elements of the greatest importance, so carbon and its oxides have been discussed in a separate chapter and its other compounds will be discussed in Topic Eight. We shall now consider the remaining elements of the family, namely silicon, germanium, tin and lead. These elements have positive valences of 2 or 4 and resemble one another somewhat in chemical behaviour. There is a marked transition from acidic to basic qualities with increasing atomic number and this group shows more progressive differences than any other group.

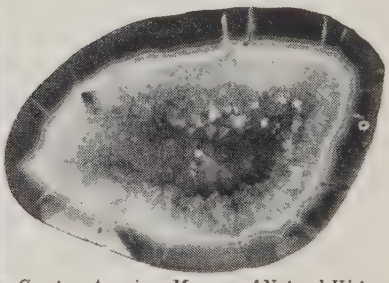
Carbon is the half-way element in the first period. As we pass from the strongly basic lithium to the strongly acidic fluorine we find a steady progression in properties which goes with an increase in the number of outer electrons. Carbon, silicon, tin and lead have four outer electrons and hence they must find ways of donating or using four more electrons to have inert gas outer shells. Carbon and silicon do this by sharing electrons with other elements but the metallic elements tin and lead give electrons to other elements to form electrovalences. We thus pass from distinct non-metals forming weak acids through amphoteric elements to the distinct metal lead. Tin is also a metal but it can show amphoteric properties.

SILICON

2. Occurrence. Silicon does not occur in nature as the free element. It is second to oxygen in abundance in the earth's crust, of which its compounds with oxygen and other elements comprise about 87 per cent. About 26 per cent of the solid crust of the earth is composed of silicon itself. The most abundant compound of silicon is the oxide, *silica*, SiO_2. This is found as sand, sandstone, the several varieties of quartz, and many other minerals as onyx, agate, jasper, flint and opal. The element is also found in granite, clay, mica, feldspar, shale, marl, asbestos, topaz and many other minerals.

From Holmes: "General Chemistry", courtesy of The Macmillan Company

Fig. 185. Natural quartz crystals.



Courtesy American Museum of Natural History

Fig. 186. Agate is hydrated silica with colloidal impurities.

The process of making glass from natural compounds of silicon has been known since ancient times. In 1669 Becher stated that silicates contained an earth, which we now know as silica, and Scheele showed in 1773 that silica acted as an acid earth. Amorphous silicon was prepared in 1823 by Berzelius; Deville prepared the crystalline variety in 1854.

3. Preparation of silicon. Silicon is produced commercially by reducing silica by carbon in an electric furnace. Care must be taken to prevent the formation of the carbide, but a fairly pure silicon may be obtained.

$$SiO_2 + 2\ C \longrightarrow 2\ CO + Si$$

If this reaction is carried out with ferric oxide mixed with the silica, an alloy of iron and silicon, known as ferrosilicon, will be produced. This alloy is used instead of silicon in the preparation of steel.

4. Properties of silicon. Amorphous silicon is a dark brown powder composed of very small crystals. The crystalline form has a structure resembling a diamond and is hard enough to scratch glass.

Silicon burns when heated with oxygen but the reaction is retarded by the formation of a protective film of oxide on the surface. It will react slowly with steam to liberate hydrogen.

$$\mathbf{Si + 2\ H_2O \longrightarrow SiO_2 + 2\ H_2}$$

Silicon reacts readily with the halogens. With fluorine the combination occurs spontaneously but with iodine both elements must be heated to a high temperature. The tetrafluoride usually is not prepared by direct union of the elements because of the difficulty of obtaining them in a pure state. It is prepared by the action of hydrofluoric acid on silica.

$$\mathbf{SiO_2 + 4\ HF \longrightarrow 2\ H_2O + SiF_4}$$

Silicon tetrafluoride is a colourless gas which fumes in moist air and hydrolyzes with water to produce hydrofluoric acid and silicic acid.

$$\mathbf{SiF_4 + 4\ H_2O \longrightarrow H_4SiO_4 + 2\ H_2F_2}$$

Part of the silicic acid precipitates as H_4SiO_4 or H_2SiO_3 (which is produced from H_4SiO_4 by the loss of H_2O), and part reacts with more hydrofluoric acid to form *fluosilicic acid*, H_2SiF_6. *Silicon tetrachloride* may be made by the action of chlorine on a heated mixture of silica and carbon, or upon silicon carbide. It hydrolyzes completely and fumes strongly in moist air.

$$\mathbf{SiCl_4 + 4\ H_2O \longrightarrow 4\ HCl + H_4SiO_4}$$

Denser fumes are made by the addition of ammonia which forms ammonium chloride with the hydrogen chloride. Mixtures of this kind are used for the production of smoke screens. Titanium tetrachloride is also used for this purpose.

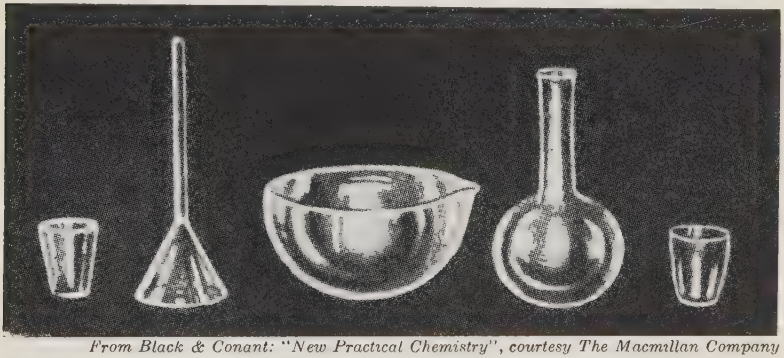
Silicon combines with sulphur, nitrogen, carbon and many metals. The compounds with metals are known as *silicides*, examples of which are FeSi (ferrosilicon), Mg_2Si and $CoSi_3$. Silicon forms several *hydrides* with hydrogen, such as SiH_4, Si_2H_2 and Si_2H_6, which are analogous to certain hydrocarbons. They ignite spontaneously in the air and react with water to liberate hydrogen and form silicon dioxide.

5. Silicon dioxide. Silicon forms two oxides, *silicon monoxide*, SiO and *silicon dioxide*, SiO_2. The monoxide is of little importance and may be prepared by reducing the dioxide with carbon under specially controlled conditions. The dioxide, known as *silica*, is one of the most important compounds in the crust of the earth. It is also found in the connective tissue of animals, in the skeletons of small organisms that live in water, known as *diatoms*, and in vegetable fibres. *Kieselguhr* or *diatomaceous earth* is a mass consisting of the siliceous skeletons of diatoms. Silica occurs in the free state and combined with various bases in the form of *silicates*. It occurs in three crystalline forms and one amorphous form.

The most common crystalline form of silica is *quartz*, which occurs in hexagonal crystals. These crystals are often coloured by various metallic oxides. Manganese produces *amethyst*; *smoky quartz* is due to the presence of carbonaceous matter; and the presence of very small air bubbles gives *milky* quartz. Pure quartz is colourless and is known as *rock crystal*. Quartz crystals are sometimes very large and one weighing nearly a ton has been discovered (see Fig. 185).

When quartz is heated to about 870°C. it changes into a crystalline form known as *tridymite*. This variety of silica crystallizes in the triclinic system and has been found in

nature. When tridymite is heated to about 1450°C. it changes into the third variety of silica known as *cristobalite*, which crystallizes in the tetragonal system. This form of silica has been found in nature in the same localities as tridymite. Both varieties are found in silica bricks which have been heated to a high temperature. Quartz has a specific gravity of 2.67 while each of the other crystalline forms has a specific gravity of 2.3.



From Black & Conant: "New Practical Chemistry", courtesy The Macmillan Company

Fig. 187. Quartz can be blown like glass to make laboratory utensils.

When quartz is heated above 1700°C. it softens gradually and forms a thick liquid. In this state it can be used to make laboratory articles such as beakers, flasks and tubing. Quartz has a low coefficient of thermal expansion, and vessels made of fused quartz can be heated to red heat and plunged into water without breaking. Quartz vessels are also resistant to all reagents except hydrofluoric acid, fused alkalis, or solutions of strong alkalis. Fused quartz is opaque because of the presence of bubbles of different gases. Clear quartz may be produced by reducing the pressure in the furnace in which it is melted. Since quartz allows the passage of ultra-violet light, it is used in mercury vapour lamps and in sunrooms where the effects of the ultra-violet portion of sunlight is desired. Quartz windows and lenses are used in apparatus where the passage of ultra-violet light is required.

Amorphous silica occurs in nature as *opal*, which may be colourless or tinted by metallic oxides. Mixtures of crystalline and amorphous silica occur in *onyx*, *agate*, *flint*, *chalcedony* and *jasper*.

Silica does not dissolve in water or acids, except hydrofluoric acid. It is the anhydride of *silicic acid*, H_4SiO_4, and it reacts with fused alkalis such as sodium or potassium hydroxides to form silicates.

In addition to the use of quartz in the manufacture of laboratory vessels, it is also used in ornaments and as threads for supporting delicate pointers in electrical instruments. Granite and sandstone are largely composed of quartz. The coarser sandstones are used as building stones and the fine-grained ones are used as grindstones and whetstones. Sand and crushed sandstone are mixed with clay and sintered together to make silica fire brick. Silica powders with a very large surface are used for filter aids, for polishing, and for the manufacture of cement, dynamite and other articles.

6. Silicic acid and the silicates. When silica is fused with sodium carbonate or treated for prolonged periods with strong solutions of sodium or potassium hydroxides it forms alkali salts which are soluble in water if the proportion of silica to alkali oxide is not too high. The solution is known as waterglass, and is described by the ratio of silica to alkali. When the ratio is 1:1 the salt is called sodium metasilicate, $Na_2SiO_3.5H_2O$, and when it is 1:2 it is sodium orthosilicate. When the latter is treated with an acid solution, orthosilicic acid, H_4SiO_4, is obtained.

$$Na_4SiO_4 + 4\ HCl \longrightarrow 4\ NaCl + H_4SiO_4$$

The silicic acids decompose rapidly into water and silica so a suspension of colloidal silica gel is produced. This gelatinous silicic acid is another example of a hydrated oxide which loses water on heating or in the presence of concen-

trated acids. An examination of the simplest formulas of the silicates would lead to the belief that the dehydration of silicic acid gel occurs in definite stages. The actual existence of specific acids is very doubtful and X-ray determinations of the structure of the silicates derived from the postulated acids fail to show any evidence of the radicals. It seems better to think of silica, SiO_2, associated with various numbers of water molecules. The silicates may be regarded as having various ratios of silica, water and the other basic radicals. For this reason both the empirical formula and the oxide composition of the compounds is given below.

There are many natural silicates which may be considered as salts of metasilicic acid. Among these are many common minerals.

Name	*Empirical Formula*	*Oxide Composition*
Wollastonite	$CaSiO_3$	$CaO.\ SiO_2$
Asbestos	$Mg_3Ca\ (SiO_3)_4$	$3MgO.\ CaO.\ 4SiO_2$
Talc	$H_2Mg_3\ (SiO_3)_4$	$3MgO.\ 4SiO_2.\ H_2O$
Beryl	$Be_3Al_2\ (SiO_3)_6$	$3BeO.\ Al_2O_3.\ 6SiO_2$

Other silicate minerals may be regarded as salts of orthosilicic acids, disilicic acids and trisilicic acids. Some of these are *olivine*, Mg_2SiO_4, *willemite*, Zn_2SiO_4, *serpentine*, $Mg_3Si_2O_7$ and *orthoclase*, $KAlSi_3O_8$. Since water, silica, and the oxides of the metals may be present in a great many different proportions the number of silicate minerals is very great.

When gelatinous silicic acid is heated to about 300°C. under reduced pressure it loses all but a small amount of its water but it retains its structure. It is called *silica gel* and it has marked adsorptive properties for water, gases and vapours.

Many artificial silicates are made for specific purposes such as waterglass, which is used as a grease remover, for preserving eggs, fireproofing, and as an adhesive. Slags are artificial silicates and so are synthetic gems, rock wool, glass and Portland cement.

7. Pottery and bricks. The term *clay* is applied to a mixture of minerals which is plastic enough to be moulded while wet, to retain its shape when dried, and to sinter together when heated to a high temperature without losing its original shape. Clay is produced in nature by the weathering of feldspars and other natural alumino-silicates. The weathering of these rocks is due to volcanic gases, waters containing organic acids from peat beds and coal beds, and water containing dissolved carbon dioxide, and it furnishes the clay in a more or less colloidal state. The clay is washed by water and may be transported for long distances by streams. During its travel it becomes associated with all kinds of material from rocks and soils over which it may pass, and transported clays are apt to be less pure than residual clays. Residual clays, after a long process of washing and settling form white *china clay* which is also known as *kaolin*.

Fig. 188. Beehive kilns in a modern Canadian brick plant.

Pottery is generally made by mixing together white clay, flint, quartz and feldspar. The mixture is moulded into the required shape and fired in a kiln at about 1000°C. This produces the *body* which is then covered with a fusible mixture of lead borosilicate, clay and feldspar, which has been well ground and mixed with water, and the articles are fired again. The melted mixture covers the surface and forms the *glaze*. The ware may be decorated by painting the body with coloured oxides before firing, by painting fusible enamels on the glaze and refiring, or by colouring the glaze itself. The chief varieties of pottery are *earthenware*, *porcelain* and *bone china*, which consist of various materials mixed with clay.

Drain pipes are made from clay containing iron so that the product is a buff or red colour. Salt is added to the kiln to produce a glaze. The salt volatilizes and the vapours attack the surface of the ware, covering it with a glass-like skin known as *salt glaze*. Fire-brick is made from refractory clays which soften at high temperatures. The bricks are moulded by hand or by machinery and are fired at about 1200°C. Ordinary building bricks are made from less refractory clays and are fired at a lower temperature.

An artificial aluminum silicate known as *ultramarine* is prepared by fusing a mixture of china clay, sodium carbonate, sulphur and some carbonaceous material. This substance has a colour varying with its composition, which is usually adjusted until the desired blue is obtained. The product is used as a pigment and for bluing. A similar substance is found in nature as the mineral *lapis lazuli*, which has a beautiful blue, green, or violet colour, and has been used for many years in decorations.

Fuller's earth is a very adsorbent variety of clay which is used as a filtering medium and a decolorizing agent in the purification of oils. It is also used as a filler in soap making.

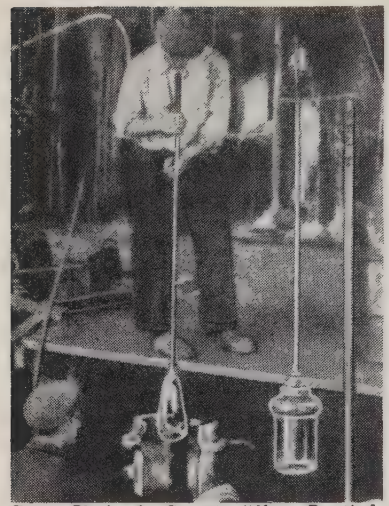


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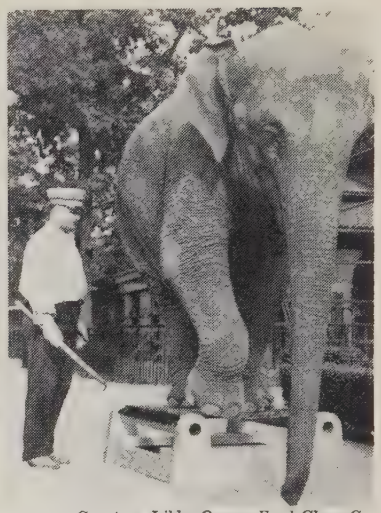
Fig. 189.



Courtesy Libby-Owens-Ford Glass Co.

Fig. 190.

Fig. 189. Glass vessels are blown in moulds.

Fig. 190. Tempered glass, three-quarters of an inch thick and three feet square, supports a 6800-pound elephant.

It derives its name from its former use in removing grease from wool, a process which is known as "fulling".

8. Glass. When silica is heated with certain salts, whose acid anhydrides are volatile, silicates are formed and the oxide of the non-metal is liberated.

$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2$$
$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$

When a mixture of sand, limestone or slaked lime, sodium or potassium carbonate, and an oxide of lead is fused, *glass* is produced on cooling. Glass is a solidified undercooled solution of several silicates, which are produced as indicated in the above reactions. The glass should be clear, brittle, and amorphous. Old glass will frequently develop a crystalline structure. When heated, glass will pass through a

wide range of temperature where it is plastic before it becomes a liquid which may be poured.

In the plastic stage the glass may be worked and moulded. After the glass has been prepared and allowed to cool to the right temperature, it may be poured into moulds or can be gathered in a ball on a blow-pipe and blown by a skilled worker into various shapes. In modern plants the glass is blown into moulds by compressed air. Window glass is made by drawing out large cylinders of glass from the furnace, cracking them, and allowing them to flatten out on tables where they may be rolled to the desired thickness. Plate glass is poured on a table, rolled to thickness, and then polished. All articles made of glass have been strained when they were shaped and if these strains are not removed the articles will be liable to crack when they are cooling. To remove these strains the glass must be cooled slowly. This process is known as *annealing* and is done by passing the glass articles through a long furnace on a moving belt. This annealing furnace is kept at a high temperature at the entrance and at a much lower temperature at the exit, and the speed of the belt is adjusted so that the glass will leave the furnace properly annealed.

Common glass, known as *soda glass*, *lime glass*, or *crown glass*, is a mixture of sodium and calcium silicates together with an excess of silica. It is used for window-panes, bottles, and other similar articles. It softens at a relatively low temperature and may be worked easily. Most laboratory tubing is made from this glass. *Hard glass*, which requires a higher temperature for working, is a potash glass. Before World War I, *Jena glass* was commonly used for scientific glassware. It is a hard glass composed of zinc and barium borosilicates. When Jena glass was shut off from America by the war, *Pyrex glass* was developed in the United States, and has now replaced the former glass for laboratory use. Pyrex glass

is a sodium-aluminum borosilicate with an excess of silica. It has a low coefficient of thermal expansion and will withstand considerable heating. *Lead glasses* have a high index of refraction and are very brilliant. They are used for making cut glass articles, imitation gems, and optical lenses. This type of glass is sometimes known as *flint glass.*

Coloured glass is made by the addition of various metallic oxides to the melted glass. Common glass is often green or yellow due to the presence of iron oxides, and this tinge may be neutralized by the addition of manganese dioxide. The colour produced by the various oxides is shown in Table 34.

TABLE 34—COLOURS PRODUCED IN GLASS BY VARIOUS SUBSTANCES

Colour	*Substances*
Blue	Cobalt oxide
Green	Chromium or copper oxides
Opaque	Stannic oxide, calcium fluoride, or boric acid
Red	Selenium oxide and colloidal silver or gold
Violet	Manganese dioxide
White	Stannic oxide, calcium fluoride, or boric acid

Safety glass is made by placing a sheet of cellulose acetate between sheets of plate glass. Quartz glass has been used for sun rooms in hospitals where it was desired to admit ultra-violet light, but inexpensive varieties of glass are produced now for this purpose. Glass bricks are used in buildings and are especially desirable in air-conditioned buildings where windows are not required. Tempered glass is plate glass which has been heated in an electric furnace and chilled by blasts of cold air. Spun glass or glass fibres, made by forcing molten glass through dies, consists of thin threads which can be woven into fabrics. This material is valuable for decorative fabrics as it has a long life and is non-flammable. Spun glass can also be used as insulation.

9. Uses of silicates. Besides their use in the manufacture of glass, bricks and pottery, silicates play an important part in industry. They are raw materials in the cement industry and silica is used as an acid flux when a basic substance is to be converted into a slag. *Asbestos* is used as an insulator and in the manufacture of fireproof building materials. *Mica* is used in stove windows, as an electrical insulator, and as artificial snow for decoration. *Soapstone*, which is very like talc, is used in talcum powder and in paints, soaps, and rubber. Artificial *zeolites* are used in water softening (see Chap. 33, sec. 11). *Rock wool* is made from natural silicates and blast furnace slag. The siliceous material is fused and allowed to fall in a thin stream into a steam blast. The stream of liquid is broken into drops, which are forced into fine threads which solidify quickly. The material is a good insulator for building purposes.

National Film Board photo

Fig. 191. Bagging asbestos fibre.

National Film Board photo

Fig. 192. Long-fibred asbestos is a silicate mineral which can be woven.

10. Germanium occurs in small amounts in the sulphide ores of zinc and is obtained in the refining of that metal. It is extremely rare and resembles tin in its properties and chemical conduct.

TIN

11. Occurrence. Tin was known to the ancients, being obtained from Britain by the Phoenicians and later by the Romans. The Latin name for the metal was *stannum*, from which the symbol "Sn" has been derived.

The most important ore of tin is the sulphide, *cassiterite*, SnO_2. Most of the deposits are in the Malay States, Indonesia, Spain, China, Bolivia and Australia. There are no important deposits in North America, although the metal is recovered from scrap tin plate in the United States.

12. Metallurgy. Tin ores are of low grade and are usually concentrated by flotation, when the heavy particles of ore settle while the lighter portions of earthy material are carried away with the froth. The concentrated ore is then roasted to remove volatile oxides and to convert metals like copper, iron and zinc into their oxides. The ore is then washed with dilute sulphuric acid to change the oxides of metals other than tin into their soluble sulphates, which are washed away. The residue is then smelted with powdered coal in a reverberatory furnace. The tin is remelted several times, during which the impurities which are less soluble remain in the ladles while the melted tin is poured away. The refined tin is cast into blocks, which are known as *block tin*. Tin may also be obtained by electrolysis.

13. Properties and uses of tin. Tin has three allotropic forms, known as *alpha*, *beta* and *gamma* tin. The usual form is the beta variety, which is a white malleable metal with a specific gravity of 7.3. Beta tin is crystalline (tetragonal) and when a rod of the metal is bent, the crystals slip over one another, producing a noise known as the "tin cry". If it is cooled below 18°C. it changes to the alpha form which is also known as *grey tin*. Grey tin crystals are cubical and the specific gravity is 5.8. This variety of tin is brittle and will crumble easily to powder. Articles made of tin are liable to

disintegrate in a low temperature because of the formation of this modification of the metal. An alloy of tin and lead is used to make solder. This alloy has a lower melting point than tin or lead and easily flows over clean metal surfaces. Zinc chloride, ammonium chloride, muriatic acid and rosin are used as fluxes to dissolve the oxide coating on the metal.

Tin is not tarnished in moist air at low temperatures but at higher temperatures it becomes coated with a layer of oxide. It reacts readily with sulphur and the halogens. It reacts slowly with dilute hydrochloric and sulphuric acids, liberating hydrogen. With concentrated hydrochloric acid it reacts rapidly. With concentrated nitric acid, metastannic acid and nitrogen dioxide are formed.

$$\mathbf{Sn + 4\ HNO_3 \longrightarrow H_2SnO_3 + 4\ NO_2 + H_2O}$$

Tin will dissolve in hot alkali hydroxides to form *stannates*.

$$\mathbf{Sn + 2\ KOH + H_2O \longrightarrow K_2SnO_3 + 2\ H_2}$$

Tin is very resistant to corrosion and is used to coat sheet iron to make the familiar *tin plate*. The sheet iron is first "pickled" by dipping it in hydrochloric acid to remove oxides, and then dipped into molten tin. The tin protects the iron from corrosion, but if the tin surface is scratched it gives no protection, since tin is lower than iron in the electrochemical series. Tin is used in many alloys such as *solder*, *pewter*, *Rose's metal*, *type metal*, *bell metal*, *gun metal* and *Britannia metal*. Since tin is very malleable it may be beaten into thin sheets to produce *tin foil*, which is used for wrapping various products. Block tin pipes are used for distilling water and other liquids.

14. The oxides and hydroxides of tin. *Stannous oxide*, SnO, is a black powder which may be prepared by heating stannous oxalate. It burns in air to produce *stannic oxide*.

Stannous hydroxide, $Sn(OH)_2$, is a white substance which may be precipitated by adding a soluble hydroxide to a solution of stannous salt. When heated it is dehydrated and forms the oxide. It is amphoteric, dissolving in acids to give *stannous salts*, and in bases to give *stannites*.

$$\mathbf{Sn(OH)_2 + 2\ HCl \longrightarrow SnCl_2 + 2\ H_2O}$$
$$\mathbf{H_2SnO_2 + 2\ NaOH \longrightarrow Na_2SnO_2 + 2\ H_2O}$$

Stannic oxide, SnO_2, which is white when cold and yellow when heated, may be prepared by burning tin or stannous oxide. If prepared at a low temperature it dissolves in acids and alkalis but when heated to a high temperature it becomes inactive. If stannic oxide is fused with sodium hydroxide *sodium metastannate*, $Na_2SnO_3.3H_2O$ is obtained. It is used as a mordant in dyeing. The stannic acid, which acts as the mordant, is produced by acidifying the solution. Cotton goods may be fireproofed by soaking them in a solution of sodium metastannate and then, after drying, placing them in a solution of ammonium sulphate. The stannic acid is too weak to give an ammonium salt and ammonia is given off.

$$\mathbf{Na_2SnO_3 + (NH_4)_2SO_4 \longrightarrow Na_2SO_4 + H_2SnO_3 + 2\ NH_3}$$

The sodium sulphate is washed out of the material and the stannic acid remains as stannic oxide. This compound cannot be washed out and the textile will remain fireproofed.

15. The chlorides of tin. *Stannous chloride*, $SnCl_2$, may be prepared by the action of tin upon hydrochloric acid. As tin has a tendency to pass into the tetravalent condition, stannous chloride can be used as a reducing agent. It reduces mercuric chloride to mercurous chloride. It is used as a mordant in dyeing and in the weighting of silk because of its ready hydrolysis.

Stannic chloride, $SnCl_4$, may be prepared by the action of an excess of chlorine upon tin. It acts like the chloride of a

non-metal, since it is a liquid with a boiling point of 114°C. which does not conduct electricity. It forms a hydrate with water, $SnCl_4.5H_2O$, and this compound is used as a mordant.

16. The sulphides of tin. *Stannous sulphide*, SnS, precipitates as a brown substance when hydrogen sulphide is passed into a solution of a stannous salt.

Stannic sulphide, SnS_2, is produced as a yellow solid when hydrogen sulphide is passed into a solution of a stannic salt.

LEAD

17. Occurrence. Lead was produced and used by the Egyptians, and the Romans used the metal for water pipes. The symbol "Pb" comes from the Latin *plumbum*. The most important ore of lead is *galena*, PbS, which occurs in association with the sulphides of silver, zinc, copper and some other minerals. Lead is also found in *cerussite*, $PbCO_3$ and *anglesite*, $PbSO_4$. The principal lead-producing countries are Spain, Australia, Germany, the United States and Canada. The most famous deposit is the Sullivan mine, near Kimberley, British Columbia.

Courtesy Consolidated Mining and Smelting Co.

Fig. 193. Burning the sulphur out of lead ores to make lead oxides.

18. Metallurgy. The lead ore is crushed, concentrated by flotation, and heated to remove part of the sulphur. The lead sulphide is changed partly into lead sulphate and lead monoxide. The ore is then heated with a mixture of fresh ore, iron ore, coke and limestone in a blast furnace. The lead monoxide is reduced by the carbon or carbon monoxide, which also reduces the ferric oxide to ferrous oxide. The limestone acts as a flux for the silica that is present in the ore.

$$PbO + C \longrightarrow Pb + CO$$
$$PbO + CO \longrightarrow Pb + CO_2$$
$$Fe_2O_3 + C \longrightarrow 2\ FeO + CO$$

The ferrous oxide reacts with the lead sulphide and lead sulphate.

$$PbS + FeO + C \longrightarrow FeS + Pb + CO$$
$$PbSO_4 + FeO + 5\ C \longrightarrow FeS + Pb + 5\ CO$$

The reaction between the lead oxide and sulphide also produces some lead.

$$PbS + 2\ PbO \longrightarrow 3\ Pb + SO_2$$

The lead drawn off from these processes is hard because it is alloyed with other metals, and is known as *lead bullion.* The bullion is heated in a reverberatory furnace in the presence of air, when the more easily oxidized metals are converted to their oxides which float on the surface and may be skimmed off. The lead is further purified by the *Parke's* or *Bett's process.* In Parke's process, zinc is added to the molten lead. The zinc dissolves the silver, gold and copper, and floats on top of the lead to form a crust which can be skimmed off. In Bett's process, first put into commercial operation in Canada, the lead is purified electrolytically. The lead bullion is formed into anodes and pure lead forms the cathode. The electrolyte is fluosilicic acid and lead fluosilicate. Gold, silver and bismuth, form an "anode mud" and metals like

iron and zinc go into solution, only the lead being deposited on the cathode.

19. Properties and uses. Lead is a soft malleable metal with a low tensile strength. When heated to a temperature just below the melting point it becomes plastic and while in that state can be made into pipes, rods and wire.

Lead is an even less active metal than tin. Its activity with reagents is decreased by the fact that the compounds which form are insoluble and make a protective coating. Hard water causes a deposit of lead carbonate and sulphate in water pipes. These substances are insoluble and strongly adherent, so that they protect the pipe from corrosion and prevent the water from becoming contaminated with lead compounds. With soft water, however, lead hydroxide is formed. This compound is somewhat soluble and, like all lead compounds, is poisonous. Lead pipes are therefore not suitable for conveying drinking water. Lead is not acted upon by dilute hydrochloric or sulphuric acids, but concentrated sulphuric acid acts upon the metal as lead sulphate is somewhat soluble in the acid. This is why very concentrated sulphuric acid cannot be prepared by the lead chamber process. Nitric acid also dissolves lead forming lead nitrate and oxides of nitrogen.

Lead has positive valences of 2 and 4, but the compounds in which it is bivalent are the more familiar. The hydroxide is amphoteric but is more basic than acidic. All lead compounds are poisonous and the results are cumulative since the elimination of the lead from the body by means of the kidneys is very slow. Great care must be taken in industry to prevent lead poisoning.

Lead has many uses because of its resistance to corrosion. It is used for waste pipes, sinks, and for making the chambers of a sulphuric acid plant. It is used as a resistant covering for cables. Large quantities are used in the manufacture of

paints and in the plates of storage batteries. It is used in many alloys as *pewter*, *shot*, *solder*, *fuse metal* and *type metal*. Lead tetraethyl is used in the manufacture of anti-knock compounds for gasoline.

20. The oxides of lead. *Lead monoxide*, PbO, is a yellow solid known as *massicot*, but the commercial product contains some red lead which turns it to a buff-coloured powder known as *litharge*. It may be made by heating lead in air. It is used in glass making, and in the manufacture of rubber goods, pottery glazes, storage batteries and paints. A mixture of litharge and glycerine is used as a cement for glass, porcelain, stone and metals.

Lead dioxide, PbO_2, is a brown powder which may be produced by the action of oxidizing agents upon lead hydroxide or red lead.

$$\mathbf{Pb_3O_4 + 4\ HNO_3 \longrightarrow PbO_2 + 2\ H_2O + 2\ Pb(NO_3)_2}$$

Red lead or *minium*, Pb_3O_4, is a bright red powder formed by heating the monoxide in air at about 475°C. It is a compound of the two oxides, PbO, and PbO_2. It is used in glass manufacture and as an orange undercoating paint for structural iron-work.

21. White lead and paint. *White lead* is *basic lead carbonate*, $Pb_3(OH)_2(CO_3)_2$. It may be precipitated from a solution of lead nitrate by sodium carbonate. *Normal lead carbonate*, $PbCO_3$, is precipitated from lead nitrate solutions by sodium bicarbonate. White lead is usually made by the *Dutch process* which has been in use for centuries. In this process lead discs, known as *buckles*, are stacked in earthenware vessels containing a shallow layer of acetic acid. The vessels are covered with boards on which manure or spent tan-bark is spread. Tiers of vessels and boards are stacked one on top of another until the shed is filled. The manure or tan-bark ferments, liberating carbon dioxide and heat,

the latter vaporizing the acetic acid. The action of carbon dioxide, water, oxygen and acetic acid upon the lead causes the production of white lead. The process requires three or four months for completion. In the *Carter process* melted lead is atomized by a blast of compressed air, and the finely divided material is placed in wooden drums containing acetic acid and carbon dioxide. White lead is produced in about two weeks. In the *French process* white lead is precipitated by carbon dioxide from a solution of basic lead acetate.

A paint usually contains three chief ingredients, the *oil*, the *body*, the *pigment*. The oil, which is usually linseed oil, hardens to a tough adherent resin as the result of oxidation by the air. The oil does not dry by evaporation so oils like linseed oil, which oxidize in this manner, are known as *drying oils*. The addition of manganese dioxide or other oxides and the boiling of the oil cause more rapid oxidation. Substances which are added to paint oils to increase oxidation are known as *driers*. The body is a fine powder which fills the paint, makes it opaque, and prevents the formation of minute pores in the oil film. White lead is the most common material for the body, but it has the disadvantage of becoming darker in colour if it is exposed to the action of hydrogen sulphide, owing to the formation of black lead sulphide. Since hydrogen sulphide is present in the smoke from most soft coal fires, paint used for interior surfaces is apt to become darker if white lead is used as the filler. Unless the paint is to be white in colour, a suitable pigment is added. Various oxides, coloured salts and lakes are used as pigments. Lakes consist of dyes adsorbed on precipitated aluminum oxide.

22. Other compounds of lead.

Lead nitrate, $Pb(NO_3)_2$, may be prepared by the action of nitric acid upon lead or lead monoxide.

Lead chloride, $PbCl_2$, *lead bromide*, $PbBr_2$ and *lead iodide*, PbI_2, may be made by the action of the corresponding halogen acid upon lead monoxide, or, since the halides are not very soluble in cold water, by precipitation.

The halides are slightly soluble in hot water. In the determination of lead in a solution, lead chloride is precipitated together with silver and mercurous chlorides. The lead chloride is dissolved by hot water in which the chlorides of silver and mercurous mercury are not soluble, and the lead chloride is separated by filtration when the solvent is cooled (see Chap. 38, sec. 7).

Lead acetate, $Pb(C_2H_3O_2)_2$, is a soluble white salt which may be prepared from lead monoxide by acetic acid. It has a sweet taste and is known as *sugar of lead*.

Lead arsenate, $Pb_3(AsO_4)_2$, is a white salt prepared by adding a solution of lead acetate to one of sodium arsenate. It is used as an insecticide.

Lead chromate, $PbCrO_4$, is a yellow salt which may be precipitated by adding a solution of potassium chromate to a solution of a lead salt. It is used as the pigment *chrome yellow*.

Lead sulphate, $PbSO_4$, is a white salt which may be prepared by adding a soluble sulphate to a solution of a lead salt. It is used as a pigment.

Question Summary

1. (*a*) What are the two sub-groups of Group IV?
(*b*) Why do we find less similarity among the elements of the silicon-tin-lead family than among the elements of other families?

2. How does silicon occur on the earth?

3. (*a*) How may amorphous silicon be prepared?
(*b*) How may crystalline silicon be prepared?

4. (*a*) What are the physical properties of silicon?
(*b*) How does silicon react with oxygen and water?
(*c*) How does silicon react with the halogens?

5. (*a*) How does silica occur in nature?
(*b*) Describe the different kinds of quartz.
(*c*) What are the uses of articles made of fused quartz?

6. (*a*) Describe orthosilicic acid and its salts.
(*b*) Describe metasilicic acid and its salts.
(*c*) Describe the condensed silicic acids and their salts.
(*d*) What are the properties and uses of silica gel?
(*e*) Describe the preparation and use of water glass.

7. (*a*) What is clay and how is it produced?
(*b*) What is china clay or kaolin?
(*c*) How is pottery made?
(*d*) How are drain pipes made and glazed?
(*e*) How are bricks made?
(*f*) How is ultramarine prepared and what are its uses?
(*g*) What is fuller's earth and what are its uses?

8. (*a*) What is glass and how is it made?
   (*b*) How is window glass made?
   (*c*) How is plate glass made?
   (*d*) What is the principle and method of annealing?
   (*e*) List the different kinds of glass and their uses.
   (*f*) How is coloured glass prepared?
   (*g*) Discuss the use of structural and spun glass.

9. Name some of the natural silicates and give their uses.

10. What are the properties of germanium?

11. Where does tin occur on the earth?

12. (*a*) How is tin obtained from its ores?
    (*b*) How is tin obtained from scrap tin?

13. (*a*) What are the properties of tin?
    (*b*) Give some of the uses of tin.
    (*c*) Name some of the important alloys containing tin.

14. (*a*) Describe the oxides of tin.
    (*b*) Describe the stannic acids.

15. What are the properties and uses of the tin chlorides?

16. Describe the sulphides of tin.

17. Where does lead occur on the earth?

18. How is lead obtained from its ores?

19. (*a*) What are the properties of lead?
    (*b*) Discuss the use of lead in water pipes.
    (*c*) Name some of the alloys containing lead.

20. (*a*) What are the uses of litharge?
    (*b*) What are the uses of lead dioxide?
    (*c*) What are the uses of red lead?

21. (*a*) What is white lead and how is it prepared?
    (*b*) Discuss the use of oil in paint.
    (*c*) Discuss the body and pigment of paint.

22. Describe some of the common salts of lead.

Chapter **36**

The Phosphorus Family

1. Introduction. If we examine the periodic table, we find in the fifth group five elements whose properties and whose compounds are so similar to one another that we may consider the elements as being in one family. These elements are *nitrogen*, *phosphorus*, *arsenic*, *antimony* and *bismuth*. Nitrogen and its compounds have already been discussed and we shall now consider the remainder of the family. All these elements have valences of 3 and 5. With increasing atomic weight we find that the chlorides are less completely hydrolyzed, the hydrides become less stable and the oxides become more basic and less acidic. Nitrogen is definitely non-metallic while bismuth is somewhat metallic in character.

PHOSPHORUS

2. Occurrence. Phosphorus was discovered in 1669 by Brand, and Scheele made it from bones in 1771. It is named from the Greek "light carrier".

Phosphorus does not occur free in nature since it is such an active element. Its most important compound is calcium phosphate, $Ca_3(PO_4)_2$, which occurs in the mineral *phosphorite*. This mineral is found in many parts of the world and appears on the market as *phosphate rock*. Calcium phosphate is found in most soils, and the element is found in the form of phosphates or organic compounds in plant structures, particularly in the seeds. Phosphorus is an important constituent of the bones and teeth, and it is found in blood and urine. Complex organic compounds of phosphorus are found in the brain, muscles and nerves.

3. Preparation of phosphorus. Phosphorus is prepared by reducing pulverized phosphate rock or bone ash with carbon in an electric furnace. Sand (silica, SiO_2) is added to produce calcium silicate which forms a slag. The sand acts as a flux and the melted slag collects at the bottom of the furnace where it may be drawn off. The furnace is shown in Fig. 194. During the formation of the calcium silicate, phosphorus pentoxide is formed as a vapour at the high temperature of the furnace.

$$2\ Ca_3(PO_4)_2 + 6\ SiO_2 \longrightarrow P_4O_{10} + 6\ CaSiO_3$$

The phosphorus pentoxide is reduced by the carbon.

$$P_4O_{10} + 10\ C \longrightarrow 10\ CO + P_4$$

The phosphorus vapour is condensed to a liquid and is separated from the carbon monoxide. The liquid phosphorus is usually run into moulds where it hardens into sticks.

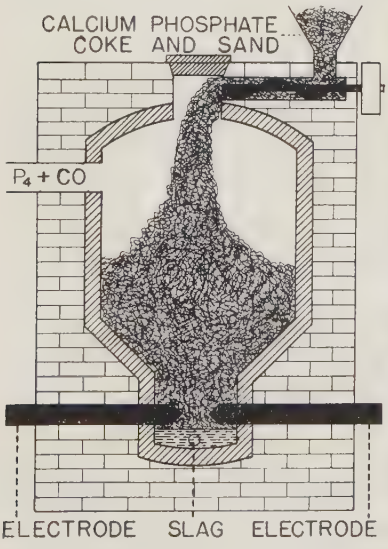


Fig. 194. Electric furnace for phosphorus.

Courtesy "Journal of Heredity"

Fig. 195. Bones are mainly calcium phosphate.

4. Properties of phosphorus. Phosphorus has several allotropic forms, the most familiar of which are *yellow* and *red* phosphorus. Yellow (sometimes called *white*) phosphorus is a soft waxy solid with a garlic-like odour. It can be cut easily with a knife. Its vapour density indicates the molecular formula P_4. It is insoluble in water, but it is soluble in some organic solvents, such as carbon disulphide and ether. It is very active chemically, combining with oxygen and the halogens at ordinary temperature. It unites with oxygen so easily that it must be stored beneath the surface of water. At room temperature it oxidizes, giving off fumes of phosphorus pentoxide; it ignites at 30°C. Light is given off during the slow oxidation and may be seen if the piece of phosphorus is placed in the dark. This emission of light is known as phosphorescence and is caused by some of the energy of the oxidation being released directly as light instead of as heat. Great care must be taken in handling phosphorus as nasty burns may be received and the vapour is very poisonous.

When yellow phosphorus is heated in the absence of air, red phosphorus is formed. This change occurs slowly at ordinary temperatures but it is fairly rapid at 200° to 300°C. Red phosphorus forms a vapour composed of molecules of P_4, and it condenses to the yellow variety. It is insoluble in carbon disulphide and it is not poisonous. It is not as active as the yellow variety and need not be kept under water. It combines with oxygen to form phosphorus pentoxide.

5. Uses of phosphorus. Phosphorus is used in making incendiary shells and in the production of smoke-screens. It is used in the manufacture of phosphor-bronze and in the preparation of the various compounds of the element such as the chlorides and the sulphide. Small quantities are used in making rat poisons. Large quantities are used in the manufacture of matches.

6. Matches. The use of phosphorus in matches depends upon the ease with which the element and its compounds can be ignited. The first matches, which were introduced about 1825, contained yellow phosphorus, but the use of that substance is now prohibited by law in all countries. Yellow phosphorus produced a decay of the bones of the jaw among the employees of the match factories, and this disease, known as "phossy jaw", often had fatal results.

The ordinary match head contains combustible substances, such as paraffin and sulphur, together with an oxidizing agent, as potassium chlorate. Fillers, such as clay or starch, are added and sometimes an abrasive material as ground glass or sand is used. The tip of the head contains phosphorus sesquisulphide, P_4S_3, which ignites when the head is rubbed against a rough surface. The combustion of this substance starts a reaction between the potassium chlorate and the sulphur, and finally the wooden stick burns. The sticks are generally dipped in a solution of alum or sodium phosphate to prevent "after glow".

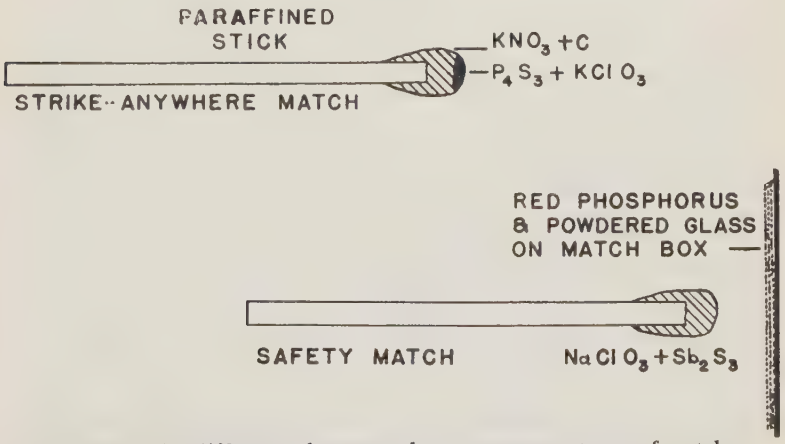


Fig. 196. The difference between the two common types of matches.

Safety matches differ from the ordinary match in that the head will not ignite unless it is rubbed against the material

provided on the side of the box. The head usually contains an oxidizing agent like potassium chlorate and a combustible substance such as antimony sulphide, Sb_2S_3. The striking surface of the box is coated with red phosphorus, an oxidizing agent, and an abrasive, bound together with glue. The friction ignites the red phosphorus which in turn sets fire to the head of the match.

7. The oxides of phosphorus. There are two well-known oxides of phosphorus, the trioxide, P_2O_3 and the pentoxide, P_2O_5, which are the anhydrides of phosphorous and phosphoric acid respectively. The simplest formulas for these oxides are P_2O_3 and P_2O_5, and these are generally used, but the actual molecular formulas seem to be double these, namely P_4O_6 and P_4O_{10}. The trioxide is formed by burning phosphorus in a limited supply of air and the pentoxide is formed by burning phosphorus in oxygen. It is a white solid which unites easily with water to form phosphoric acid.

$$\mathbf{P_2O_5 + 3\ H_2O \longrightarrow 2\ H_3PO_4}$$

Because of the ease with which this oxide unites with water, it is frequently used as a dehydrating agent, especially for drying gases.

8. Phosphine, PH_3, corresponds to ammonia, NH_3. Like ammonia, it reacts with hydrogen chloride to produce a salt, phosphonium chloride, PH_4Cl. Phosphine is a very poisonous gas, with an offensive odour. Usually it is prepared by heating a concentrated solution of sodium hydroxide in which particles of yellow phosphorus are suspended. Air must be removed from the generator. Phosphine is a colourless gas which is decomposed easily by heat into its elements and is very poisonous. It is insoluble in water and thus forms no compound corresponding to ammonium hydroxide.

9. The phosphorus halides. Phosphorus combines with all of the halogens by direct union of the elements. The most important of the halides are the chlorides, PCl_3 and PCl_5. The trichloride is a fuming colourless liquid, and the pentachloride is a yellow solid. They are used in the preparation of organic compounds. Both of them react vigorously with water to form hydrochloric acid and an acid of phosphorus.

$$PCl_3 + 3\ H_2O \longrightarrow 3\ HCl + H_3PO_3$$
$$PCl_5 + 4\ H_2O \longrightarrow 5\ HCl + H_3PO_4$$

You will remember that similar reactions were used for the preparation of hydrobromic and hydriodic acids (see Chap. 28, sec. 10 and sec. 15).

10. The phosphoric acids. There are three phosphoric acids representing different degrees of hydration of the anhydride, but in each case the valence of phosphorus is the same. The relation between these three phosphoric acids and the hydration of the anhydride may be seen by the following table.

TABLE 35—THE PHOSPHORIC ACIDS

Acid	*Equation showing hydration*
Metaphosphoric acid, HPO_3;	$P_2O_5 + H_2O \longrightarrow 2\ HPO_3$
Pyrophosphoric acid, $H_4P_2O_7$;	$P_2O_5 + 2\ H_2O \longrightarrow H_4P_2O_7$
Orthophosphoric acid, H_3PO_4;	$P_2O_5 + 3\ H_2O \longrightarrow 2\ H_3PO_4$

Metaphosphoric acid, HPO_3, is a white glassy solid which may be melted and cast into sticks. It is known in commerce as *glacial phosphoric acid*. Sodium metaphosphate is a stable salt which may be fused to a glassy solid. The oxides of certain metals dissolve in this glass giving it a characteristic colour which may be used to identify the metal. In analysis, a bead of sodium metaphosphate is fused on the end of a platinum wire. When this bead is dipped in certain salts and heated in a flame, the oxide of the metal of the salt is formed and dissolves in the bead. In the case of cobalt oxide, a mixed phosphate, $NaCoPO_4$, is formed which gives a blue colour to the bead. Sodium hexametaphosphate, $(NaPO_3)_6$, is a water-conditioning agent used in dishwashers and boiler water to remove calcium and other ions which cause hardness in water.

Pyrophosphoric acid, $H_4P_2O_7$, is a white crystalline solid. Although it is a tetrabasic acid, it only forms the secondary and normal pyrophosphates, as $Na_2H_2P_2O_7$ and $Na_4P_2O_7$. The other salts are not known.

Orthophosphoric acid, H_3PO_4, usually known as *phosphoric acid*, is the most important of the phosphoric acids. The

commercial article is prepared by the action of excess sulphuric acid upon calcium phosphate, in the usual method of preparing an acid.

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 \longrightarrow 3\ CaSO_4 + 2\ H_3PO_4$$

The acid may also be produced by adding air to the vapour of phosphorus during its preparation. This produces phosphorus pentoxide which may be dissolved in water.

Orthophosphoric acid is tribasic and the three salts are known. The sodium salts and their names are as follows:

NaH_2PO_4	Monosodium phosphate, primary sodium phosphate, or dihydrogen sodium phosphate.
Na_2HPO_4	Disodium phosphate, secondary sodium phosphate, or monohydrogen sodium phosphate.
Na_3PO_4	Trisodium phosphate, tertiary sodium phosphate, or normal sodium phosphate.

Normal sodium and potassium phosphates are strongly hydrolyzed in solution, giving the secondary phosphate and the hydroxide.

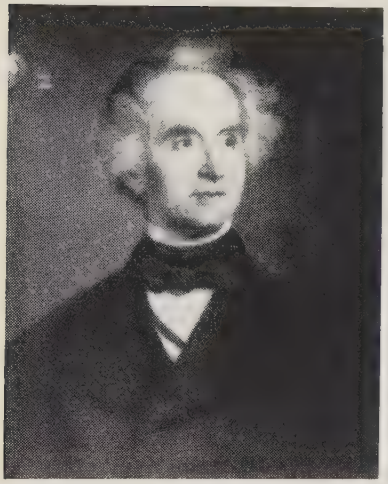
$$Na_3PO_4 + H_2O \longrightarrow NaOH + Na_2HPO_4$$

Because of this production of sodium hydroxide, trisodium phosphate is used as a cleaning agent. Its solutions are more basic than those of sodium carbonate.

When normal calcium phosphate is heated with less sulphuric acid, primary calcium phosphate is produced.

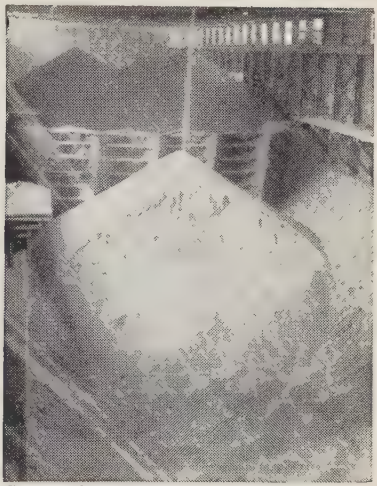
$$Ca_3(PO_4)_2 + 2\ H_2SO_4 \longrightarrow 2\ CaSO_4 + Ca(H_2PO_4)_2$$

This phosphate, known as *superphosphate*, is much more soluble than the normal calcium phosphate and is used as a fertilizer. For this use the calcium sulphate is not removed but forms part of the fertilizer. It is usually made to contain 20 per cent of its weight of P_2O_5. By using phosphoric acid triple superphosphate, free from calcium sulphate, is produced.



Courtesy Fisher Scientific Co.

Fig. 197.



Courtesy Consolidated Mining and Smelting Co.

Fig. 198.

Fig. 197. Justus von Liebig (1803-1873), German chemist, laid the foundations for modern agricultural chemistry.

Fig. 198. Ammonium phosphate fertilizer.

11. Phosphorous acid. The phosphoric acids have been shown to be related to phosphorus pentoxide. In a similar way, phosphorous acid is related to phosphorus trioxide. This oxide reacts with water to form *orthophosphorous acid*, H_3PO_3, which is commonly known as *phosphorous acid*.

$$P_2O_3 + 3\ H_2O \longrightarrow 2\ H_3PO_3$$

Phosphorous acid is usually prepared by the hydrolysis of phosphorus trichloride, tribromide, or triodide, and evaporation of the solution.

$$PCl_3 + 3\ H_2O \longrightarrow 3\ HCl + H_3PO_3$$

Phosphorous acid is a weak acid. Only the primary and secondary salts are known. The sodium salts, NaH_2PO_3 and Na_2HPO_3, the phosphites, are used in medicine. The acid is a powerful reducing agent, and will precipitate some metals, such as gold and silver, from solutions of their salts.

ARSENIC

12. Occurrence. Arsenic occurs in the free state and in a large number of minerals. It is found as the oxide, *arsenolite*, As_2O_3; the sulphides, *orpiment*, As_2S_3, *realgar*, As_2S_2, *arsenopyrite*, FeAsS, and *cobaltite*, CoAsS; and the arsenides, *arsenical iron*, $FeAs_2$ and *kupfernickel*, NiAs. Since pyrites contains some arsenic, the element is found in smoke from coal containing pyrites, and in sulphuric acid made from sulphur dioxide obtained from pyrites. Metals obtained from sulphide ores usually contain some arsenic and it may be obtained from the dust which is produced when those ores are roasted.

Arsenic was known to the ancients. It was used as a poison, and brightly coloured compounds of the element were used as pigments. The element was prepared by Albertus Magnus in 1250; and Brand showed that "white arsenic" was the oxide of arsenic.

13. Preparation of arsenic. Arsenic is usually prepared by reducing the trioxide with powdered charcoal.

$$\mathbf{As_2O_3 + 3\ C \longrightarrow 3\ CO + 2\ As}$$

Some arsenic may be obtained from furnaces where arsenopyrite is roasted.

$$\mathbf{FeAsS \longrightarrow FeS + As}$$

Considerable quantities of arsenic are obtained from the dust that collects in the flues of copper ore smelters.

14. Properties of arsenic. Arsenic is a dark grey crystalline solid which resembles a metal, but may be broken easily into small pieces. It sublimes readily giving a yellow poisonous vapour with a garlic odour. It occurs in different allotropic forms, but grey arsenic is the only one of any importance and the others are very unstable, changing into the grey form even at ordinary temperatures. It has a specific gravity of 5.7, which is higher than that of most metals.

Arsenic combines with oxygen slowly at ordinary temperatures in moist air, but at about 200°C. it burns to form the trioxide, As_2O_3. It unites directly with the halogens to form trihalides and it combines directly with sulphur. It unites with some metals to form *arsenides*. It does not displace hydrogen from acids.

15. Uses of arsenic. Arsenic is used in the manufacture of bronzes and other alloys, in the preparation of arsenic compounds, and in the making of lead shot. In the manufacture of shot, the molten lead is allowed to drop through a screen from the top of a tower. As the drops of lead fall they solidify in spheres to form the shot. The addition of arsenic to the lead lowers the freezing point and delays the solidification until the drop has assumed a spherical shape. The presence of arsenic in an alloy increases the hardness, strength and lustre, and makes the alloy more resistant to chemical action.

16. The oxides of arsenic. *Arsenic trioxide*, As_2O_3 or As_4O_6, is a white powder commonly known as *white arsenic* or *arsenic*. It may be obtained by burning the element in the air or by roasting arsenical ores. It is slightly soluble in cold water and is more soluble at higher temperatures. It is extremely poisonous and is the substance usually involved in cases of arsenical poisoning. By increasing the dosage gradually, some people become tolerant to arsenic and can consume quantities which would normally be fatal. Arsenic eating was once a fashionable fad. Arsenic is used in the manufacture of poison for rats, in insecticides, for wood preservants, in glass making and in dyeing. Some of its compounds are used in medicine, such as *salvarsan*, which is used in the treatment of syphilis.

Arsenic pentoxide, As_2O_5 or As_4O_{10}, cannot be made by burning arsenic in an excess of air. It may be prepared by heating arsenic acid, of which it is the anhydride.

$$2\ H_3AsO_4 \longrightarrow As_2O_5 + 3\ H_2O$$

17. Arsine. Arsenic forms a compound with hydrogen which is analogous to phosphine and ammonia, called arsine, AsH_3. Arsine may be prepared by the action of atomic hydrogen upon a compound of arsenic. This is usually done by adding the arsenic compound to a hydrogen generator which is using zinc and hydrochloric acid. Arsine is a poisonous gas with a garlic odour. It burns with a blue flame, depositing arsenic and forming water. It does not react with water and is not soluble in it.

The widely used test for the presence of arsenic, *Marsh's test*, depends upon the production and decomposition of arsine. The apparatus used in this test is shown in Fig. 199.

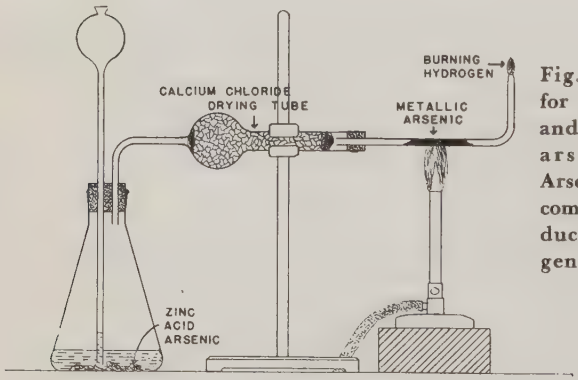


Fig. 199. Apparatus for the generation and decomposition of arsine or stibine. Arsenic or antimony compounds are reduced by the freshly generated hydrogen.

Hydrogen is generated in the flask by means of zinc and hydrochloric acid, dried by calcium chloride in the drying tube, and burned at the jet. The substance to be tested is introduced into the flask through the thistle tube. If arsenic is present, arsine will be formed and carried along with the stream of hydrogen. If the tube is heated between the drying tube and the jet, the arsine will be decomposed and arsenic will be deposited in the form of a bright metallic mirror.

$$4\ AsH_3 \longrightarrow As_4 + 6\ H_2$$

18. The arsenious acids. An aqueous solution of arsenic trioxide acts as a weak acid. It probably contains *orthoarsenious acid*, H_3AsO_3, *pyroarsenious acid*, $H_4As_2O_5$, and *metaarsenious acid*, $HAsO_2$. None of these acids have been isolated, since the evaporation of the solution produces arsenic trioxide, but salts of the acids are known. Sodium and potassium

arsenites are soluble in water but the arsenites of the heavy metals are insoluble.

The most important arsenites are the copper salts, *Scheele's green*, $CuHAsO_3$ and *Paris green*, $Cu_4(C_2H_3O_2)_2(AsO_3)_2$, once widely used as insecticides.

19. The acids of pentavalent arsenic. When arsenious acid is oxidized by concentrated nitric acid, *orthoarsenic acid*, H_3AsO_4, is produced and may be obtained by evaporation as a white deliquescent solid, $2\ H_3AsO_4.H_2O$. Salts of this acid, of *pyroarsenic acid*, $H_4As_2O_7$ and of *metaarsenic acid*, $HAsO_3$, are known. The calcium and lead salts of orthoarsenic acid are the most important and are used in insecticides.

20. Insecticides and fungicides. Insecticides are used to destroy or repel insects, while fungicides are used to prevent the growth of parisitic plant growths such as smut or mildew. The insecticides are usually stomach poisons such as arsenic compounds or contact poisons such as DDT or rotenone, but they may be repellents such as naphthalene or dichlorobenzene. Insecticides which are sprayed or dusted on vegetation must adhere well to the foliage; they must be

National Film Board photo

Fig. 200. Spraying pear trees with a fungicide to prevent blight.

relatively insoluble in rain water and they must be soluble in the digestive juices of the insect. For example, calcium arsenate is more soluble than lead arsenate so it is only used on hardy plants like potatoes or on apples in conjunction with Bordeaux mixture, which decreases its solubility.

Emulsions of mineral or coal tar oils in water are very effective contact poisons for the eggs of insects or mites such as the European red mite.

Fungus diseases are usually controlled by copper or sulphur compounds. The most common one was discovered at Bordeaux in France in 1882 when grape vines were sprinkled with lime and copper sulphate to discourage theft. The downy mildew was suppressed where the mixture was used. If lime and sulphur are boiled together a dark red solution of polysulphides is obtained. It also acts as an insecticide against some scale insects.

Synthetic organic compounds are being introduced as insecticides and fungicides. They are extremely toxic substances and should be handled with great care. Parathion is even more toxic than DDT. Hexachlorobenzene is used for insects such as the grasshopper. Rotenone has been in use for a long time against warble flies, fleas and lice on livestock. Extracted from derris root, it was the arrow poison of the Malay natives. Pyrethrum is extracted with kerosene from a daisy-like flower which grows in the Mediterranean countries and Japan. It is used in household sprays for flies in the same way as DDT.

ANTIMONY

21. Occurrence and preparation. Antimony occurs free and in combination with other elements in various parts of the world. The principal ore is the sulphide, *stibnite*, Sb_2S_3. Antimony sulphide was known to the ancients by whom it was used as a medicine and for darkening the

eyebrows. It was known to the Arabians as *kohl*. A complete description of the element and its properties was given in the book *The Triumphant Chariot of Antimony* ascribed to a fifteenth-century monk named Basil Valentine.

Antimony may be prepared from stibnite by melting it with iron.

$$3\ Fe + Sb_2S_3 \longrightarrow 2\ Sb + 3\ FeS$$

The molten ferrous sulphide is lighter than the liquid antimony and floats on the top so that the two substances are separated easily. Antimony can also be obtained by roasting the sulphide in the air to convert it to the oxide and then reducing the oxide with carbon.

$$Sb_2O_3 + 3\ C \longrightarrow 3\ CO + 2\ Sb$$

22. Properties of antimony. Antimony is a silver-white crystalline substance with a melting point of 630°C. and a specific gravity of 6.7. It is more metallic in appearance than phosphorus or arsenic, but it is very brittle and is a poor conductor of electricity.

Antimony does not combine with oxygen at low temperatures; however, at a higher temperature it burns. It combines directly with the halogens and sulphur. It does not displace hydrogen from hydrochloric acid, but it reacts with nitric acid to form antimony trioxide.

Antimony is used extensively in alloys. Lead containing some antimony is harder than ordinary lead, and is used in the manufacture of bullets, bearings and the plates of storage batteries. An alloy containing antimony tends to expand when it solidifies and is used in type metal which must fill the mould tightly. An alloy of antimony with tin and copper makes an anti-friction metal called *babbitt metal*. *Britannia metal* is a similar alloy. Some kinds of pewter are alloys of tin and lead with antimony.

23. The oxides of antimony. *Antimony trioxide*, Sb_2O_3, is a white insoluble substance. It is amphoteric in character, reacting with acids to give salts of antimony, and with bases to give *antimonites*.

Antimony tetroxide, Sb_2O_4, is formed when antimony trioxide is heated and some of it is produced when antimony is burned in air.

Antimony pentoxide, Sb_2O_5, is a yellow substance formed by heating *antimonic acid*, H_3SbO_4.

24. Stibine, SbH_3, is the compound of antimony and hydrogen. It is a poisonous gas similar to arsine but it is less stable. It may be produced by the action of atomic hydrogen as in the case of arsine. In Marsh's test, any antimony that is present will cause the deposit of a mirror that is similar to the one produced by arsine, but it is blacker in colour and is insoluble in sodium hypochlorite which will dissolve the mirror produced by arsine.

25. Other compounds of antimony. Halides are formed by the direct union of antimony and the halogens. The trichloride hydrolyzes with water to form a basic chloride.

$$\mathbf{SbCl_3 + 2\ H_2O \longrightarrow Sb(OH)_2Cl + 2\ HCl}$$

The basic chloride breaks up to give water and antimony oxychloride.

$$\mathbf{Sb(OH)_2Cl \longrightarrow H_2O + SbOCl}$$

If antimony trioxide is heated with a solution of potassium bitartrate, $KHC_4H_4O_6$, a basic salt, $K(SbO)C_4H_4O_6$, known as *tartar-emetic* is formed. This salt is used as an emetic in medicine and as a mordant in dyeing.

Antimony trisulphide, Sb_2S_3, is found in nature as the black crystalline *stibnite* and may be precipitated from solutions of antimony salts as an orange-red solid.

$$\mathbf{2\ SbCl_3 + 3\ H_2S \longrightarrow Sb_2S_3 + 6\ HCl}$$

Antimony pentasulphide, Sb_2S_5, may be precipitated from solutions of pentavalent antimony.

BISMUTH

26. Occurrence and preparation of bismuth. Bismuth occurs free in nature, and also as *bismite*, Bi_2O_3, and *bismuthenite*, Bi_2S_3. It may be prepared by roasting the sulphide to form the oxide and reducing the oxide by charcoal.

27. Properties and uses of bismuth. Bismuth is a greyish-white crystalline metal with a reddish tinge. It reacts slowly

with oxygen to form the trioxide at ordinary temperatures and a film of the oxide protects the element from further action. It combines directly but not vigorously with sulphur and the halogens. It dissolves readily in nitric acid to form the nitrate. This formation of the nitrate shows the definite metallic character of bismuth.

Bismuth is used in the preparation of low-melting alloys. *Newton's metal* melts at 94.5°C. *Rose's metal* melts at 93.8°C. *Wood's metal* melts at 60.5°C. These alloys are used for electric fuses, automatic sprinkler systems and for automatic fire doors. In the event of a local rise of temperature, a plug made of the alloy melts, thus releasing water or operating a fire-resistant door.

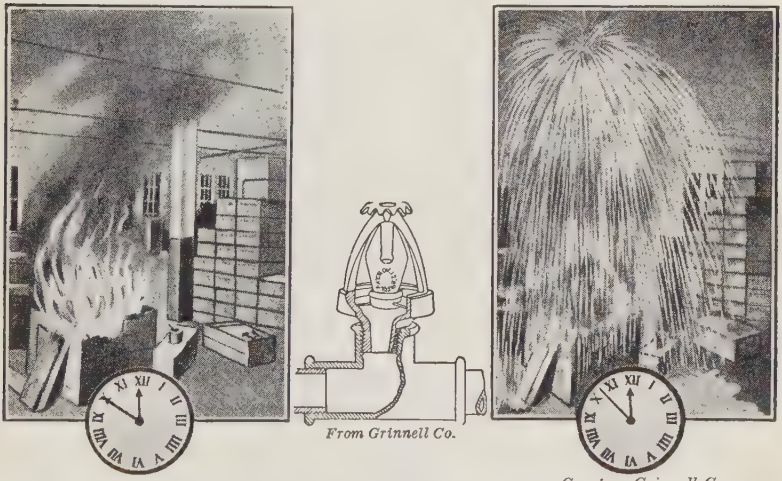


Fig. 201. A low-melting alloy of bismuth holds water in the sprinkler.

28. Compounds of bismuth. *Bismuth trioxide*, Bi_2O_3, is a yellow solid formed by burning the element. This oxide dissolves in acids and produces normal salts which hydrolyze easily to form basic salts.

$$BiCl_3 + 2\ H_2O \longrightarrow Bi(OH)_2Cl + 2\ HCl$$
$$Bi(NO_3)_3 + 2\ H_2O \longrightarrow Bi(OH)_2NO_3 + 2\ HNO_3$$

Basic bismuth nitrate is known as *bismuth subnitrate* and is used in medicine. The basic chloride decomposes to form the oxychloride.

$$Bi(OH)_2Cl \longrightarrow H_2O + BiOCl$$

The oxychloride is known as *pearl white* and is used in face powders as a pigment.

29. Summary of periodic properties.

TABLE 36—SOME PROPERTIES OF THE PHOSPHORUS FAMILY

Property	*Nitrogen*	*Phosphorus*	*Arsenic*	*Antimony*	*Bismuth*
Atomic Weight	14.008	30.98	74.91	121.76	209.0
Density of solid	1.026	1.82	5.73	6.68	9.80
Valence	1, 2, 3, 5	3, 5	3, 5	3, 5	3, 5
Hydride	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Stability of Hydride	Very Stable	Less Stable	Little Stable	Unstable	Very unstable
Trioxide in Water	Strong Acid	Weak Acid	Very weak acid	Ampho-teric	Basic
Pentoxide in Water	Strong Acid	Moderate Acid	Very weak acid	Insoluble	Acid
Colour of Sulphide	.....	Yellow	Yellow	Orange	Brown
Hydrolysis of Chlorides	(Explosive)	Acid	Acid	Oxy-chloride	Oxy-chloride

There is a gradual transition from acidity to basicity as the atomic weight increases. At the same time there is usually a gradual transition in the physical properties of the compounds. The formulas of the compounds are alike and their reactions are very similar, being modified mainly in degree. The phosphorus family shows some of the most closely related properties of any family except the alkalis and the halogens.

Question Summary

1. Name the members of the phosphorus family.
2. How is phosphorus found in nature?
3. How may phosphorus be prepared?
4. What are the properties of phosphorus?
5. What are the uses of phosphorus?
6. (*a*) How are matches manufactured?
   (*b*) Why is yellow phosphorus no longer used in matches?
7. What oxides does phosphorus form?
8. What is phosphine?
9. What is the reaction between the chlorides of phosphorus and water?
10. (*a*) How are the phosphoric acids related?
    (*b*) Name the salts of orthophosphoric acid.
    (*c*) What is superphosphate and how is it prepared?
11. Discuss phosphorous acid.
12. How does arsenic occur in nature?
13. How is arsenic prepared?
14. What are the properties of arsenic?
15. What are the uses of arsenic?
16. Describe arsenic trioxide.
17. (*a*) How is arsine prepared?
    (*b*) Describe Marsh's test for arsenic.
18. Describe the acids of trivalent arsenic.
19. Describe the arsenic acids.
20. What are the types of insecticides and fungicides?
21. (*a*) Where does antimony occur in nature?
    (*b*) How is antimony prepared?
22. (*a*) What are the properties of antimony?
    (*b*) What are the uses of antimony?
23. Describe the oxides of antimony.
24. How is stibine prepared?
25. Discuss some other compounds of antimony.
26. How does bismuth occur and how is it recovered?
27. (*a*) What are the properties of bismuth?
    (*b*) What are the uses of bismuth?
28. Discuss the reactions of bismuth trioxide.
29. Prepare several generalizations about the physical properties and chemical behaviour of the members of the phosphorus family.

Chapter **37**

Nuclear Transmutations

1. The change of one element into another. Ever since the first alchemist dreamed of changing lead into gold, men have been tantalized by the possibility of transforming elements into more valuable ones. When radioactivity was discovered a new method by which this could be accomplished appeared possible. If atoms would disintegrate spontaneously it indicated that transmutation could at least occur. Investigation showed that ordinary influences such as heat, pressure, electric and magnetic fields, or light had no effect on the rate of such changes. The door to transmutation was still closed.

A careful study of radioactivity and the emanations associated with it at least led to an understanding of how disintegrations might occur. When Becquerel discovered radioactivity in 1896, thorium and uranium were the only ones of the present list of radioactive elements which had been isolated. By 1898, Pierre and Marie Curie had discovered two new elements, radium and polonium, and their success inspired others to seek such elements.

2. Radioactive disintegration theory. A revolutionary explanation was proposed for such spontaneous disintegration by Rutherford and Soddy in 1902.

1. The atoms of a radioactive element are unstable.

2. Such unstable atoms will explode or disintegrate, ejecting light-weight particles and energy while forming a new atom in the process.

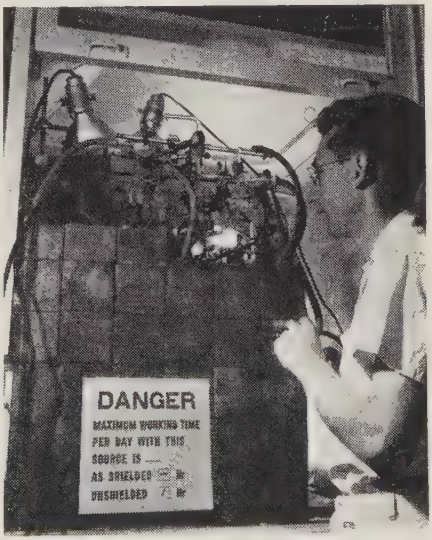
3. This disintegration is not affected by any physical factor outside of the atom.

The time required for half the atoms of any radioactive element to disintegrate is called the half-life. It is independent of when the measurement is started and can be calculated from the rate of decay which is measured by the number of particles ejected per second. Those atoms which have a large probability of disintegration are very short-lived and we cannot expect to find them in nature. Radium has a half-life of 1590 years which is very short in the age of the earth, so it is a very rare element. Thorium and uranium require billions of years to decay so they are found in greater abundance, while actinium which is very active exists only in minute amounts.

The naturally occurring radioactive atoms always expel either an alpha particle or an electron when they disintegrate. The energy adjustment is made by the emission of gamma

Courtesy Fisher Scientific Co.

Fig. 202.



National Film Board photo

Fig. 203.

Fig. 202. Artist's conception of the discovery of radium.

Fig. 203. Protected by a thick wall of lead bricks, a scientist at the Atomic Energy Plant prepares radioactive isotopes.

rays and electrons are lost or captured by the planetary electron systems to form new atoms. When an alpha particle is thrown out of radium (atomic weight 226, atomic number 88), it represents the loss of four units of weight and two positive charges. A new nucleus is formed with an atomic weight of 222 and an atomic number of 86. The reduced nuclear charge will allow the two outer electrons of radium to disappear at the same time, leaving an inert gas, radon. The amount of transmutation product is very small because the half-life of radium is very long compared to the time which an experimenter can wait, but Sir William Ramsay collected and weighed a small sample in 1909. He obtained a value of 223 for the weight of 22.4 litres at S.T.P. The alpha particles had already been shown to pick up electrons to form helium so the Rutherford-Soddy theory was completely verified.

Radium ⟶ Radon + Helium + Energy

Almost exactly one hundred years after Dalton's theory of

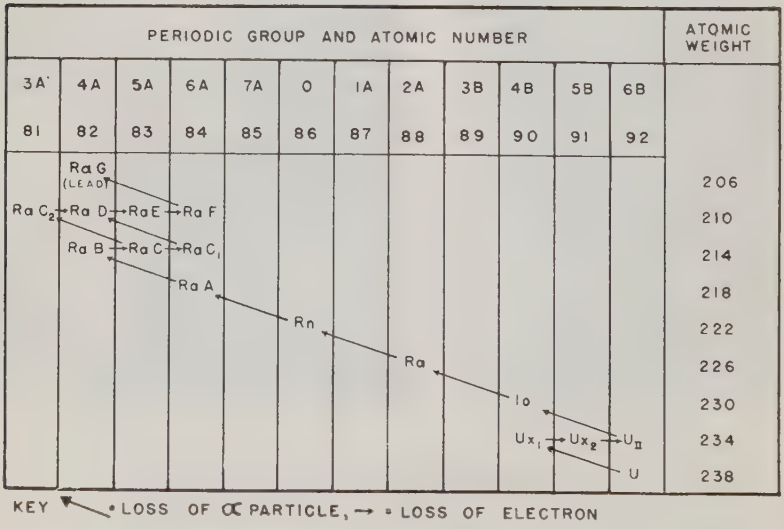


Fig. 204. Periodic table changes in the disintegration of uranium.

indestructible atoms was accepted, men agreed that some atoms could transform themselves into other atoms.

The general behaviour of naturally radioactive atoms when they lose sub-atomic particles is summed up in the radioactive disintegration law which says: *When an atom loses an alpha particle it moves two places to the left in the periodic table and when it loses an electron from the nucleus it moves one place to the right* (see Fig. 204).

3. Artificial radioactivity. The nuclear atomic model of an atom may be likened to a giant able to swing many balloons about him at one time but only having a few different lengths of string. The balloons represent the planetary electrons and the giant represents the nucleus. The lengths of the strings determine the orbits of the balloons. The room required by the circling balloons on the longest strings is the volume inside which other systems of circling balloons cannot penetrate. In order to hit the giant it is necessary to use a pea-shooter or a BB gun shooting a particle which is very much smaller than the spaces in the system. Unless your aim is good most of your pellets will go through the empty spaces without striking the giant at all. If you use a pea-shooter your pellets may be turned back by the giant's outer covering because they do not have enough energy, but if you use a more powerful gun they will be able to tear right through into the giant's body.

The same considerations apply to the smashing of atoms. The tiny compact nucleus can only be attacked with sub-atomic bullets of terrific energy. Alpha particles were the first of such bullets to be available to scientists but they were relatively large and slow. Because of their positive charge they were repelled by the positive nucleus. They could sometimes penetrate to the nucleus of a light atom but they could not be accurately directed toward the target and it was like shooting at distant ducks with a machine-gun firing in all

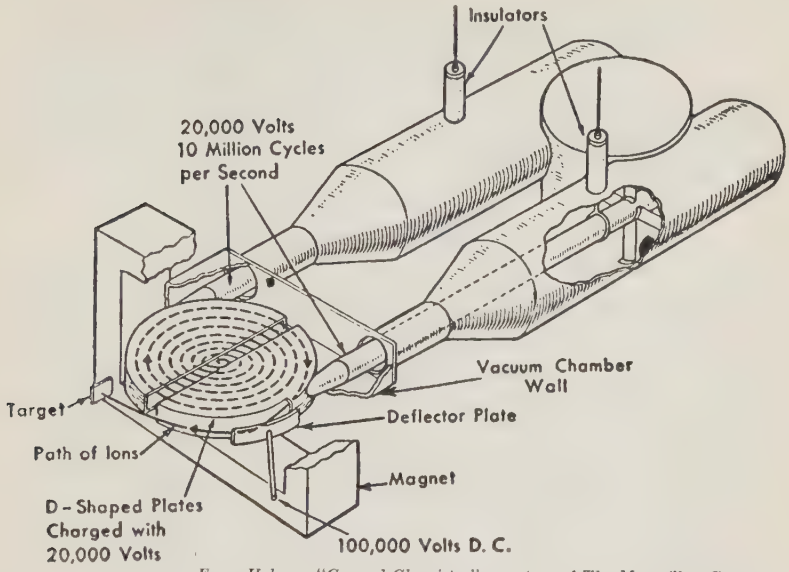
directions. Rutherford carried out the first transmutation in 1919. He bombarded nitrogen with α particles and placed a screen beyond the range of the α particles. A few scintillations were observed as much as 40 cm. from the source. He showed that these particles had the same ratio of charge to mass as protons. Such long-range protons were not found when oxygen or hydrogen was used so it was assumed that they arose from the nuclear reaction.

$$^{14}_{7}\mathrm{N} + ^{4}_{2}\mathrm{He} \longrightarrow ^{1}_{1}\mathrm{H} + ^{17}_{8}\mathrm{O}$$

The fact that nitrogen was converted into an isotope of oxygen was demonstrated by the fog tracks of the atoms in a Wilson Cloud Chamber. Many other light elements were found to give off protons and become new elements when the nucleus was struck by an alpha particle.

In 1934 Curie and Joliot noticed that light atoms such as aluminum and magnesium continue to emit radiation after being bombarded with alpha particles. Aluminum yielded radioactive phosphorus and magnesium yielded radioactive silicon with half-lives of only two or three minutes. These discoveries opened up a whole field of nuclear chemistry where new atoms of every kind are created and their half-lives measured.

4. Producing and using high-speed particles. Atoms can be smashed by high-speed particles such as neutrons, protons, and deutrons as well as by alpha particles. Recent advances in electrical engineering have made it possible to obtain effects equal to voltages of many hundred millions of volts and to accelerate charged particles to speeds approaching that of light. One of these instruments is the *electrostatic generator* which charges a large conducting sphere. Another is the *cyclotron* which accelerates charged particles by keeping them going in a circle with a huge magnetic field while the



From Holmes: "General Chemistry", courtesy of The Macmillan Company

Fig. 205. The cyclotron accelerates protons every half revolution.

voltage is kept continuously opposite in sign by a high-frequency oscillating current. The betatron and the syncrotron are newer devices for accelerating electrons sufficiently to enable them to be used for atom smashing. The uranium or plutonium pile is a source of neutrons of unprecedented quantity and intensity. The range of the most intense of these particles runs into miles of air.

The tools for nuclear reactions are:

Alpha particles from radioactive materials.

Neutrons from light elements and atomic piles.

Protons from positive rays in hydrogen.

Deuterons from positive rays in deuterium.

Electrons from radioactive materials, heated filaments, cathodes and other sources.

Each tool may be used for special types of atomic transmutation. The type of change produced by *alpha rays* has been described above. Elements with atomic weights as much

as four units greater than the parent element may be produced if the addition is successful. Usually neutrons are ejected from the newly formed nucleus so the isotope is only three units larger in atomic weight. The conversion of boron into nitrogen thirteen and a neutron is a good example.

$$^{10}_{5}\mathrm{B} + ^{4}_{2}\mathrm{He} \longrightarrow ^{13}_{7}\mathrm{N} + ^{1}_{0}\mathrm{N}$$

Neutrons are very effective because being without charge they can penetrate to the nucleus without having a high velocity. Slow neutrons are extremely useful because like a magnetic or acoustic mine they are attracted into the nucleus by the gravitational attraction of its mass. In this way they are self-aimed at the target and being uncharged they have no barrier to surmount in reaching it. A vast number of *neutron reactions* are known of which the conversion of aluminum to sodium and helium is a good example.

$$^{27}_{13}\mathrm{Al} + ^{1}_{0}\mathrm{N} \longrightarrow ^{24}_{11}\mathrm{Na} + ^{4}_{2}\mathrm{He}$$

Radioactive nitrogen, $^{13}_{7}\mathrm{N}$, and radioactive carbon, $^{13}_{6}\mathrm{C}$, are obtained by bombarding carbon with *high-speed protons*.

$$^{12}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H} \longrightarrow ^{13}_{7}\mathrm{N} \text{ then } ^{13}_{7}\mathrm{N} \longrightarrow ^{13}_{6}\mathrm{C} + \text{positron}$$

5. Mass changes and nuclear energy. Since elements are constructed of protons, neutrons, alpha particles and electrons it should be possible to calculate their atomic weights from the masses of these constituents. A simple case shows the discrepancy which can arise in such attempts. The atomic weight of hydrogen, which consists of one proton and one electron, is 1.008. Helium should consist of four protons and four electrons if these are the basic units, which would give it an atomic weight of 4.032, but its actual atomic

weight is only 4.030. This difference in weight is due to the energy involved in packing the sub-atomic particles into the nucleus. It is known as the *packing loss.*

Matter and energy are conceived to be two forms of the same thing. They are interconvertible according to the Einstein equation.

$$\mathbf{E = mc^2}$$

In this famous equation E is the energy, m is the mass, and c is the velocity of light (186,000 miles per second). The amount of energy which appears when *one pound* of matter disappears thus comes to the stupendous value of over 4×10^{23} ergs or about 450×10^8 kilowatt hours. This is enough heat to raise twenty thousand million gallons of water from the freezing point to the boiling point—an amount of water which would fill a lake 12 square miles in area about ten feet deep.

Here then is the source of the so-called *atomic energy* which is really *nuclear energy.* The disintegration of certain atoms can yield other atoms which have less total mass than the parent atom so there is a large liberation of energy. If some means could be found to use the sub-atomic particles from one atom to cause the disintegration of a second atom the process would be spontaneous and the chain would continue until all of the given mass of matter was transmuted into other elements.

6. Uranium fission. In 1934 the Italian physicist Fermi observed that uranium was converted into other elements when bombarded by slow neutrons. About 1938 it was shown that it was the *uranium 235* isotope which disintegrated and *produced several new neutrons from each atom.* It had long been known that neutrons could be slowed down by small atoms with the nuclei close together such as the hydrogen and carbon atoms in paraffin, the hydrogen and oxygen in water or the carbon atoms in graphite. Deuterium oxide

(D_2O), heavy water, was particularly good because of the high concentration of nuclei it offered to slow down neutrons.

Joliot and Curie succeeded in starting a chain reaction in uranium in 1940 but it soon died out because too many neutrons escaped. The process quickly became a war secret and the Allied Nations were fortunate in being able to offer research opportunities to the world's leading nuclear scientists. These scientists were able to work out the details which made possible the atomic bomb. Processes were developed for concentrating the uranium 235 isotope in ordinary uranium and for perpetuating the chain reaction at the desired time. One set of fission possibilities is shown in Fig. 206.

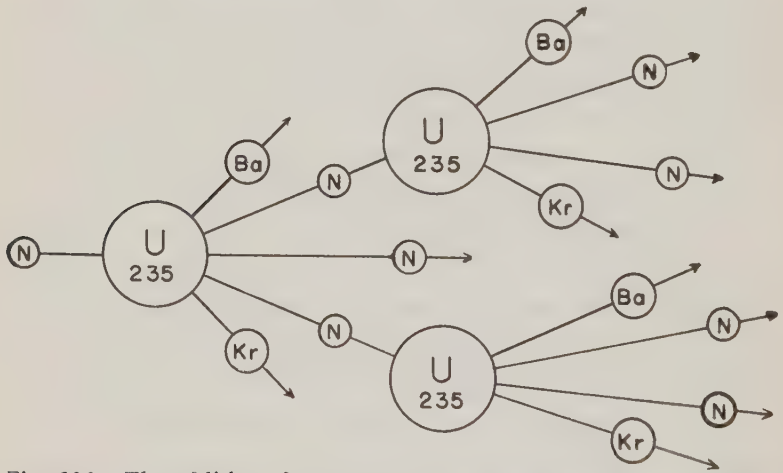


Fig. 206. The addition of a neutron to uranium liberates vast quantities of energy and causes disintegration.

7. Neptunium, plutonium, americium and curium. If the neutrons emitted by uranium 235 are slowed down they may be captured by uranium 238 to give short-lived uranium 239. This isotope does not split apart but loses an electron to give element 93 which is called *neptunium*.

$$^{238}_{92}\mathrm{U} + ^{1}_{0}\mathrm{N} \longrightarrow ^{239}_{92}\mathrm{U} \longrightarrow ^{239}_{93}\mathrm{Np} + \mathrm{e}^{-}$$

Neptunium has a short life and soon loses another nuclear electron to give element 94 or *plutonium* which has a rather longer half-life and can be separated from uranium by chemical means since it is a *different* chemical substance.

$$^{239}_{93}\mathrm{Np} \longrightarrow {}^{239}_{94}\mathrm{Pu} + \mathrm{e}^{-}$$

Plutonium captures slow neutrons like uranium 235 and can maintain a chain reaction in suitable masses.

Plutonium is produced in so-called atomic piles such as the one at Chalk River, Canada. Heavy water or graphite is used to slow down the neutrons from uranium 235. Huge volumes of ordinary water are used to absorb the heat energy produced when large numbers of neutrons, α rays, β particles and electrons are slowed down or stopped. Cadmium rods absorb the excess neutrons and control the speed of the reaction. A large enough mass of uranium must be used to perpetuate the reaction which is started by stray neutrons from the air. Some of the uranium is converted into plutonium; this is then separated by the fractional crystallization of suitable salts.

The problem in making an atomic bomb is to keep the plutonium or uranium 235 subdivided into small masses and then to bring them together at the critical moment. Some idea of the energy liberated by the fission of the nuclei with the loss of only a very small amount of the total mass may be gained from the statement that one bomb is equivalent to 20,000 tons of T.N.T.

By bombardment of uranium 238 with high-speed alpha particles from a cyclotron, Glenn T. Seaborg and his associates produced a new element, No. 95, which they called *americium*, Am. Under similar bombardment plutonium yielded traces of an extremely radioactive element, No. 96, named *curium*, Cm. These new elements, together with the

synthetic production of other elements either extremely rare or missing in nature, have completed a roster of over 96 elements for the periodic system parade. Over five hundred isotopes of these elements are now known and new ones are being continually discovered. This is the nuclear age in chemistry.

Question Summary

1. Describe briefly the discovery of some of the more important radioactive elements.

2. (*a*) State the essential postulates of the modern disintegration theory.

(*b*) What is meant by the half-life of an element? Would the half-life give any indication of its probable abundance? Explain.

(*c*) Describe the material results of an atomic disintegration. Which of the rays are most dangerous?

(*d*) State the displacement law for the periodic changes and illustrate it with examples.

3. Describe briefly how artificial radioactivity may be induced in atoms. Give examples.

4. (*a*) Name and give the source of some of the high-speed particles used to smash atoms.

(*b*) Give examples of some of the types of atomic transformations now possible.

5. What is the origin of the so-called atomic energy?

6. How does nuclear fission make the atomic bomb possible?

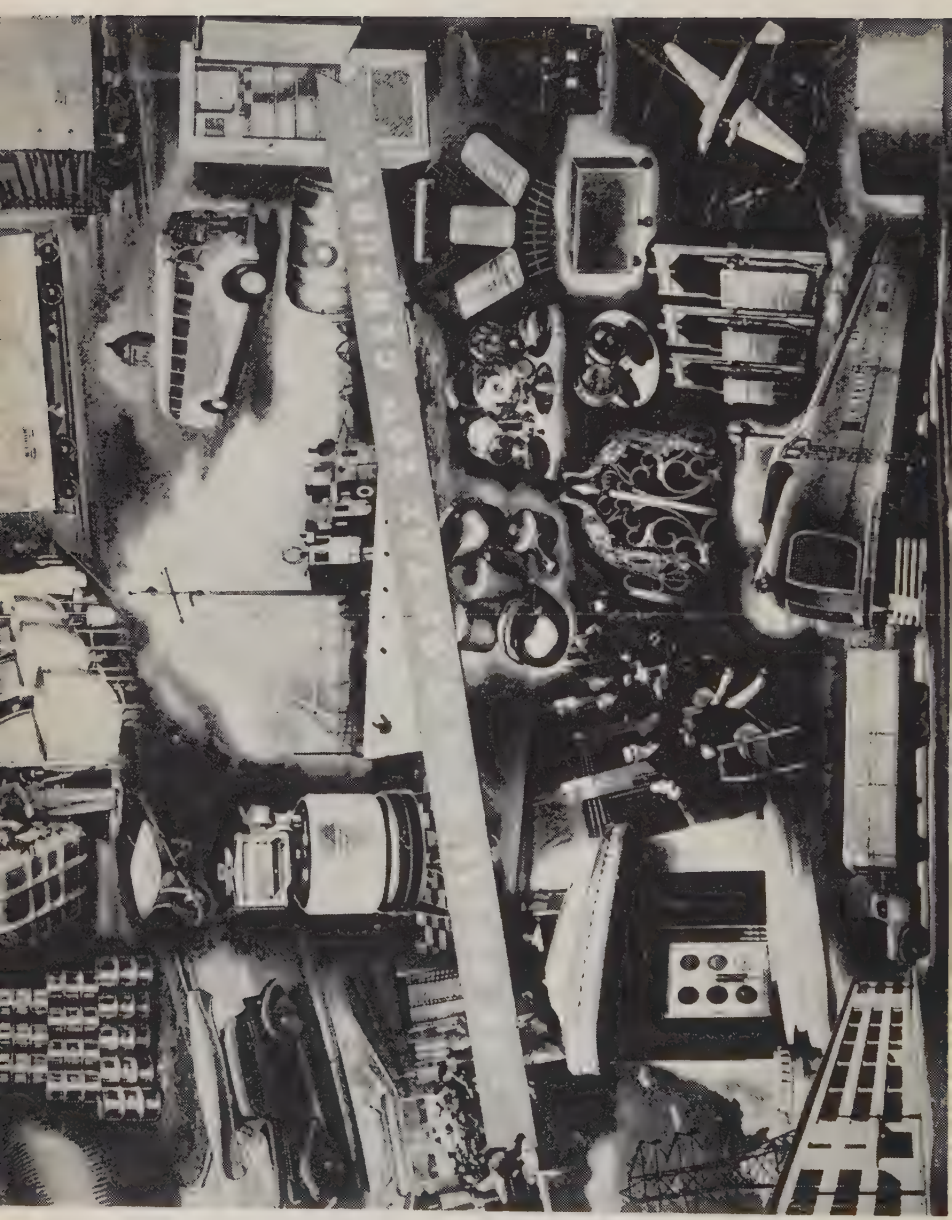
7. Describe the formation of neptunium, plutonium, americium and curium.

Topic Seven

MORE MAGIC METALS

Today we are at the height of the age of metals. The more chemically active metals as well as tin and lead have already been mentioned in other topics and the remainder are mentioned here. Many of the metals have been known for a very long time but a few of them are newcomers to the field of everyday use. Copper and bronze, being the easiest to smelt, were known to the Egyptians. Iron was more difficult to use but much superior in properties so it became the great servant of man. Silver and mercury were the playthings of the alchemists and gold has stirred men's minds and hearts throughout the ages.

The story of how metals are discovered, extracted from the earth and processed to make them ready for fabrication is the saga of our great mining and metallurgical industry. The chemical behaviour of the metals and of their compounds is the basis of the improved methods of detection, estimation, extraction and purification which make possible the recovery of so much metal with so little labour.



Courtesy Aluminum Co. of Canada

Chapter **38**

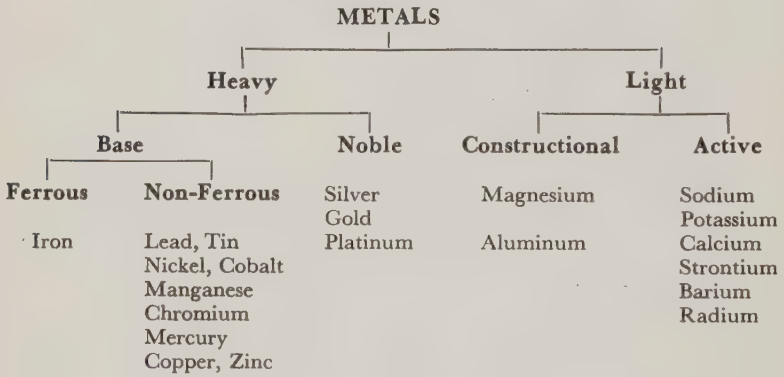
The Metals

1. Introduction. We have tried to help you to understand many general principles and now we wish you to see how they are turned to the service of man. As we study the methods of obtaining and using metals we will see many simple physical and chemical principles used repeatedly. We will see oxidation, reduction, electrolysis, density, solubility and almost all the fundamental terms of chemistry used again and again. This is *applied science* and no one can understand it thoroughly unless he has a good grasp of pure science. Every branch of applied science has its own terminology so we will have to learn a few new terms for chemical compounds and processes.

2. Properties of metals. Metals are the basis of modern civilization. Look about you and you see either metal objects or objects fashioned by means of metals. We have learned that *metals are those elements which form basic oxides* and have certain other physical properties which make them particularly serviceable. Their *metallic lustre*, if preserved, makes them very attractive because they reflect light smoothly from a polished surface. Their remarkable deformability without loss of strength enables them to be drawn in fine wires or rolled and pounded into thin sheets or a hundred other forms. We say they are *ductile* when they can be drawn into fine wires and *malleable* when they are readily made into thin sheets. Copper is one with a high ductility and gold has a remarkable malleability.

The metals are in general *good conductors of heat and electricity* (see Fig. 207), and at the same time they possess remarkable mechanical strength. They resist being pulled apart or they have *great tensile strength.* Most of them have a *considerable compressive strength* and many of them can be given great *hardness.* Some can be deformed and they will return to their original shape or they have a *large modulus of elasticity.* Lastly they have the ability to withstand repeated stresses and shocks or they have *endurance.*

3. Classification of metals. The engineer carefully measures and considers these properties in the various forms of construction. The seventy metals are usually classified as *heavy* metals if they have a density of more than 5 grams per cubic centimetre, and *light* metals if they are less dense. The more important ones may be classified as follows:



We have already discussed the light metals as well as tin and lead in the previous topic as we took up the characteristic groups of the periodic system. These elements all had complete inner shells of 2, 8 or 18 electrons. The heavy metals we wish to discuss in this topic belong to the transition element families and they have incomplete electron shells. This gives them greater cohesive strength, hardness and

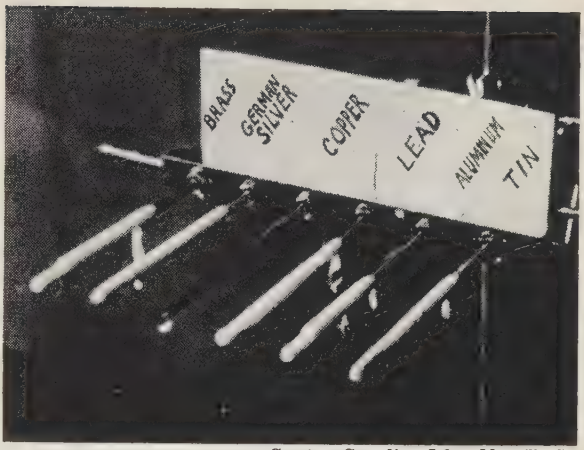


Fig. 207. Some metals conduct heat better than others. One end of each bar is in the steam chest and all were covered with wax.

Courtesy Canadian Johns-Manville Co.

elasticity than the metals of the characteristic groups. They are our major materials of metallic construction. Each is useful for a special purpose but may have disadvantages for other uses. The heavy metals are more chemically inert than the light metals and they are usually more ductile, more malleable, and much stronger. The seventy metals are combined in a multitude of ways to give *alloys* with special properties.

4. Metals in nature. The seventy metals form thousands of compounds with the non-metals and radicals. In order to understand the discovery, occurrence and recovery of metals it is necessary to have an accurate knowledge of:

(1) the relative stability of compounds;
(2) the relative solubility of compounds;
(3) the electrochemical series;
(4) oxidation and reduction.

You have had information about these factors throughout the book but it may be possible to give you a better idea of how they work together.

We have discussed the occurrence of elements before we discussed their other properties without trying to account

for the existence of these forms in nature. To exist in nature a compound of an element must be:

(1) stable to heat;

(2) insoluble and unhydrolyzed in water.

There are two types of origin for natural compounds. One is from the molten magmas of the earth's crust and the other is deposition from solution.

Now the *stability* of a compound refers to the energy required to remove some element or elements from its structure. This energy may be heat energy, radiant energy, chemical energy or electrical energy. The stability to heat is proportional to the heat of formation of the compound from its elements. In general, the farther the metal is above oxygen in the combined activity series, the more stable is the oxide formed (see Table 38). For example, lime, CaO, is one of the most stable oxides. The lighter and more active metals form very stable oxides, while the heavier and more noble metals form very unstable oxides. Since oxygen and sulphur are so nearly alike the same is approximately true of the sulphides, except that the sulphides of the very active metals are more or less completely hydrolyzed by water.

5. Solubility rules. The most important compounds of the metals are the oxides, hydroxides, sulphides, carbonates, sulphates, silicates, phosphates, chlorides and nitrates. The oxides are all insoluble, as such, and only dissolve by reacting with water to form hydroxides. In the following table certain general rules are illustrated in detail.

All the metal ions cannot be listed in this small table but you can learn these rules:

(1) Most alkali and ammonium salts are soluble.

(2) The nitrates and acetates are all soluble.

(3) The chlorides, bromides and iodides are all soluble except those of silver, lead and mercurous mercury.

(4) The sulphates are all soluble except those of calcium,

TABLE 37—THE SOLUBILITY OF METALLIC COMPOUNDS IN WATER

Compounds of	Na, K, NH_4^+, Mg, Ca, Sr, Ba, Al, Zn, Fe, Cu, Sn, Pb, Hg_2^{++}, Ag
Hydroxide	Soluble | Insoluble
Sulphide	Soluble | Hydrolyzed | Insoluble
Carbonates	Soluble | Insoluble
Sulphate	Soluble | Insoluble | Soluble | Insoluble
Silicate	Soluble | Insoluble
Phosphate	Soluble | Insoluble
Chloride	Soluble | Insoluble
Nitrate	Soluble
Acetate	Soluble

strontium, barium, lead, silver and mercurous mercury.

(5) The silicates, phosphates, hydroxides and carbonates are all insoluble except those of the alkalis and ammonium.

(6) The sulphides are all insoluble except those of the alkalis and those which are hydrolyzed.

The solubilities vary greatly as you saw in Chap. 21, and these rules are very general summaries.

You will soon notice that the form in which a metal occurs in nature is related to its activity, its solubility, and the stability of its compounds. The very active metals occur as soluble compounds in the waters of the earth or in the remnants of evaporated lakes or inland seas. Since sodium chloride is a very stable compound we usually find sodium in this form. Its oxides and sulphides are too reactive to exist in the native state. Since the calcium and barium sulphates and carbonates are stable to moderate heat and water as well as being rather insoluble it is not surprising to find these elements in such forms as limestone, gypsum and barite (barium sulphate). The moderately active metals form insoluble oxides and sulphides which are stable to water and heat so they commonly occur as compounds of these

elements. Metals as little active as copper, silver, gold and platinum may occur in the free or *native* state.

Any very insoluble form of an element is likely to occur in nature whether it be the pure metal, its oxide, its sulphide, or its ternary salt. The metals are formers of basic oxides which are neutralized by acidic oxides to form salts. The most abundant acidic oxides in nature are silicon dioxide and carbon dioxide so where high temperatures were involved *silicates* have been formed and in solutions near the carbonated surface atmosphere the hydrated basic oxides have formed *carbonates*. Since phosphates are most insoluble in very alkaline solutions we only find *phosphates* of the most active elements such as calcium. As only a limited number of metals form insoluble chlorides or sulphates we find these in nature only for such metals. Two factors tend to reduce the abundance of hydrated oxides. They are easily dehydrated by elevated temperatures and they absorb acidic oxides readily to form carbonates, silicates and phosphates.

6. The electrochemical series. There is an *activity series* of the metals where the most active metals are at the beginning and the least active ones at the end (see Chap. 22, sec. 11). There is a similar but less well defined series for the non-metals. It is possible to write the non-metal series with the most metal-like elements at the top. If we put these two series after one another we have a series with the strongest reducing agent at the top and the strongest oxidizing agent at the bottom. Table 38 is really a displacement series of the metals followed by a displacement series of the non-metals which reads non-metallic behaviour from the bottom up since they are listed in terms of their metallic behaviour.

The relationship between forms of occurrence and activity is shown in a separate column of Table 38. The very active metals form hydroxides instead of oxides and these are neutralized by the various acid radicals to form the salts.

TABLE 38—AN ACTIVITY SERIES OF THE COMMON ELEMENTS

Element	*Readily Attacked by*	*Molar Potential*		*Occurrence*	*Ease of Reduction*
Potassium	Water	−2.92	Decreasing Activity as Metals →	In soluble and insoluble salts; chlorides, nitrates, carbonates sulphates, etc.	Very difficult. Reduced by electrolysis of fused oxide, hydroxide or chloride
Barium		−2.90			
Calcium		−2.87			
Sodium		−2.71			
Magnesium	Hot water	−2.40			
Aluminum	Dilute non-oxidizing acids (HCl)	−1.70			Reduced by metals or electrolysis
Manganese		−1.10			
Zinc		−0.76		As insoluble oxides, sulphides carbonates etc.	
Chromium		−0.60			
Iron		−0.44			Oxides are reduced by carbon or hydrogen
Cadmium	Strong hot HCl	−0.40			
Nickel		−0.22			
Tin		−0.13			
Lead		−0.12			These are easily reduced from oxides
Hydrogen	HNO_3 or hot conc. H_2SO_4	0.00			
Antimony		+0.00		Free or combined in oxides sulphides etc.	
Bismuth		+0.20			
Copper		+0.34			
Silver		+0.80			Reduced by heat alone
Mercury		+0.80			
Platinum	HNO_3+ HCl	+0.86		Mainly free	
Gold		+1.36			
Arsenic	Oxides dissolve in alkalis			Occur combined with metals	
Tellurium					
Carbon					
Sulphur				Combined in soluble and insoluble binary and ternary salts	
Iodine		+0.54			
Bromine	Many binary salts are soluble in water	+1.09	Increasing Non-Metallic Behaviour →		
Oxygen		+1.23			
Chlorine		+1.36			
Fluorine		+2.81			

The ocean and evaporated inland seas now buried underground contain the most soluble salts where these were concentrated by evaporation from leaching solutions, mainly rain-water.

The ease of reduction is really a measure of stability and shows that the most active metals form anhydrous compounds which are hard to reduce to the free metal. The farther down the series we find a metal the easier it is to reduce its oxide. The industrial processes of reduction are discussed in the next chapter.

When we speak of displacement of one metal by another we mean that the reduction of the metal farther down in the series and the simultaneous oxidation of the more active metal proceeds spontaneously. Oxidation and reduction were discussed in Chap. 32, sec. 9, with examples which showed that the more active metal gives up electrons to become oxidized. This series shows by means of the potentials the tendency of the different metals to give up electrons when compared to hydrogen.

The direct combination of metals with non-metals is, of course, an example of oxidation and reduction as when chlorine is used to recover tin from used tin cans. There are other cases, as when sulphides are oxidized to sulphates by atmospheric oxygen or free metals are corroded.

The most important use of the activity series is in the study of how to prevent corrosion. If a metal is plated with one which is above it in the series the plate will all corrode away before the base metal is attacked. This is the case when steel is galvanized with zinc. On the other hand if a metal lower in the series is plated on steel as soon as a pinhole appears in the plate the active metal beneath the plate will corrode. The rusting of the familiar tinned steel cans is the best example of such action. The activity series is thus the basis of understanding these oxidation-reduction phenomena.

The activity also determines the type of solvent to be used to dissolve the free metal as shown in Table 38. The more active metals react with water, the moderately active ones dissolve in dilute acids, while the less active ones require oxidizing acids such as nitric and concentrated sulphuric acid. The noble metals are dissolved best by aqua regia which is one part of nitric acid with three parts of hydrochloric acid. The activity series is thus an invaluable guide to understanding the behaviour of the metals.

7. Detection of metal compounds. The discovery of valuable metal compounds in the field depends on the skill of the geologist or prospector in recognizing the naturally occurring compounds of the different metals. This often is very difficult because of the deceptive appearance of certain minerals. The oldest and most famous deceiver is iron pyrite, FeS_2, or "fool's gold". It has the bright yellow colour of gold and the uninitiated are easily fooled. For this reason the geologist and prospector rely upon field tests and chemical analysis to determine with certainty the nature and quantity of the valuable components. Some of these tests have been mentioned in various places in the book but we will collect them together here.

Field testing consists mainly of careful examination, measurements of density and hardness, simple chemical reactions and blow-pipe tests. The density is easily found by using Archimedes' Principle. The hardness is usually determined by the ability of various materials to scratch the mineral. The simple chemical tests are done by using drops of dilute acids and other reagents on the surface. A carbonate or sulphite will effervesce, a sulphide may reveal its presence by a faint odour of rotten eggs if it is at all soluble in the acid and other compounds may yield coloured ions. Such tests are seldom conclusive but they serve to eliminate doubts or confirm suspicions about the nature of the compound. Some

compounds have characteristic tastes and odours which also assist in their identification.

The blow-pipe is a little metal tube with a fine point used to deflect a candle or alcohol lamp flame in a tiny torch onto the surface of a lump of charcoal or plaster. The outside of the flame has excess oxygen and combines heat with oxidation so that sulphides may be converted to oxides. The inner green portion is a reducing agent and may reveal the presence of the very inactive metals. With sufficient heat many carbonates are decomposed to oxides and these are tested with cobalt nitrate or borax. Sometimes the oxide is dissolved in acid and the solution tested by the colour it gives to a flame or by its chemical reactions.

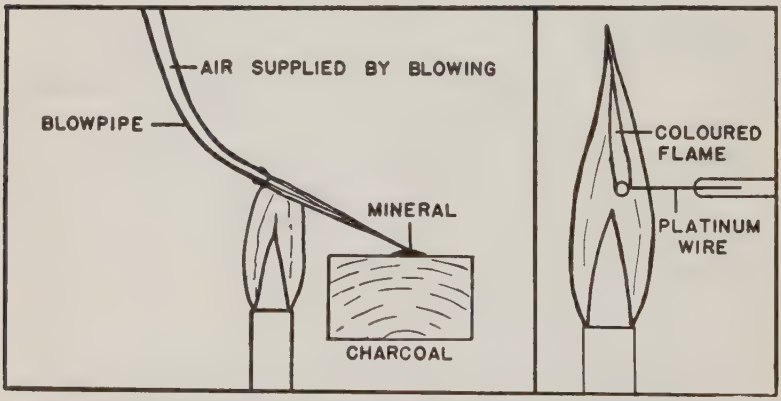


Fig. 208. Blow-pipe and flame tests are used to identify metals.

TABLE 39—FLAME TESTS FOR METAL IONS

A clean platinum or inert metal wire is dipped in a solution of the metal ion and then heated in an oxidizing flame.

Metal ion	*Flame colour*	*Metal ion*	*Flame colour*
Sodium	Yellow	Strontium	Red
Potassium*	Violet	Barium	Pale green
Calcium	Brick red	Copper (Cl^-)	Green

*A cobalt glass will absorb the yellow light waves from sodium and permit the violet light from heated potassium to be seen.

When the sample is sent into the laboratory suspected compounds may be isolated and tested or the whole sample may be ground very fine and analysed. If only the presence or absence of elements is determined it is called qualitative analysis. The metal ions which do not form insoluble chlorides are separated into groups mainly by means of the solubility of their sulphides.

Since hydrogen sulphide is only slightly ionized the concentration of sulphide ion in any saturated solution of it can be regulated by the acidity of the solution (see Chap. 25, sec. 10). The sulphides of the metals will precipitate when the concentration of the metal ion times the concentration of the sulphide ion exceeds a definite small value which is different for each sulphide. If the concentration of acid in a solution of a metal compound is regulated to about 0.3 M by HCl and the solution is saturated by passing H_2S into it the sulphides which precipitate and their colours are:

HgS	—	black	Bi_2S_3	—	brown
PbS	—	black	As_2S_3	—	yellow
Ag_2S	—	black	Sb_2S_3	—	orange
CuS	—	black	SnS_2	—	yellow

If these are filtered out of the solution and the filtrate is neutralized with ammonium hydroxide and again saturated with H_2S so that ammonium sulphide is present to yield a high concentration of sulphide ion, the less insoluble sulphides will precipitate. Those separating and their colours are:

FeS	—	black	NiS	—	black
ZnS	—	white	CoS	—	black

Since aluminum and chromium sulphides are completely hydrolyzed their hydroxides separate.

$Al(OH)_3$ — white gel. $Cr(OH)_3$ — blue-green gel.

When the solution is acidified by adding HCl before the H_2S is added the insoluble chlorides of silver, lead and

TABLE 40—TESTS FOR IONS IN COMPOUNDS

Ion	*Test*	*Observation*
Ammonium NH_4^+	Warm with NaOH	Odour of ammonia Moist red litmus turns blue
Aluminum Al^{+++}	Add NH_4OH and NH_4Cl	White gelatinous precipitate which dissolves in ammonia
Bromide Br^-	Add chlorine water Shake with CS_2 or CCl_4	Free bromine appears red-brown in CS_2 or CCl_4 layer
Chloride Cl^-	Add $AgNO_3$ and a little HNO_3	White curdy precipitate which dissolves in ammonia
Carbonate $CO_3^=$	Add dilute acid Pass gas into limewater	Limewater becomes milky
Copper Cu^{++}	Add NH_4OH slowly	A pale blue precipitate which dissolves to give a royal blue solution
Ferrous Fe^{++}	Add potassium ferricyanide	Dark blue precipitate (Turnbull's blue)
Ferric Fe^{+++}	Add NH_4OH	A red-brown gel insoluble in excess NH_4OH
Iodide I^-	Add chlorine water Shake with CS_2 or CCl_4	Free iodine appears violet in in CS_2 or CCl_4 layer
Lead Pb^{++}	Add HCl, filter cold Dissolve precipitate, add potassium chromate	$PbCl_2$ needles separate Dissolved in hot water they give yellow $PbCrO_4$.
Nitrate NO_3^-	Add fresh $FeSO_4$ Place conc. H_2SO_4 beneath	Brown ring at junction with dense H_2SO_4 layer
Silver Ag^+	Add NaCl and HNO_3	White curdy precipitate which dissolves in ammonia
Sulphite $SO_3^=$	Add HCl, pass gas through very dilute $KMnO_4$	Sharp odour of SO_2 and $KMnO_4$ decolorized
Sulphide $S^=$	Add HCl, pass gas over moist lead acetate paper	Odour of rotten eggs, metallic black film on paper
Sulphate $SO_4^=$	Add $BaCl_2$ and HCl	White precipitate of $BaSO_4$
Phosphate $PO_4^{\equiv}$	Add $MgCl_2$ and strong NH_4OH	White precipitate of $MgNH_4PO_4$ slowly forms
Zinc Zn^{++}	Add H_2S to ammoniacal solution	White precipitate of ZnS

mercurous mercury separate out and they are filtered out and tested. The common metal ions are thus separated into groups which may be further separated and the individual ions detected.

These groups are:

(1) The insoluble chlorides of Ag, Pb and Hg_2^{++}.

(2) The sulphides insoluble in acidified H_2S solutions.

(3) The metal ions precipitated by ammonium sulphide.

(4) The metal ions which are not precipitated by hydrogen sulphide, namely the alkalis and alkaline earths.

The detection of the individual ions in a mixture of salts is a complicated procedure and we can only summarize certain tests in tabular form (see Table 40).

Question Summary

1. Try to distinguish between applied science and pure science.

2. (*a*) Give the chemical definition of a metal.

(*b*) State briefly the meaning of the following terms: lustre, ductile, malleable, tensile strength, hardness.

3. (*a*) Classify the following metals as: (*i*) light or heavy (*ii*) active, base or noble.

Calcium, tin, silver, gold, sodium, iron, copper, barium.

(*b*) What difference in electronic structure exists between the metals of the characteristic sub-groups (A families) and those of the transition elements (B families)?

4. (*a*) What factors determine whether a given compound will be found in nature?

(*b*) How is the stability of binary compounds related to the activity of their elements?

5. (*a*) Write *S* after each of the following compounds which is appreciably soluble in water. NaCl, Ag_2SO_4, $Ni(OH)_2$, Ca_3PO_4, Al_2SO_4, PbS, K_2CO_3, Hg_2Cl_2.

(*b*) Explain the probable reasons for the natural occurrence of $BaSO_4$, NaCl, $CaCO_3$, PbS, Au, Fe_2O_3.

6. (*a*) Construct an oxidation-reduction series of the following metals and non-metals where the strongest reducing agent is at the top and the strongest oxidizing agent is at the bottom: bismuth, hydrogen, sodium,

potassium, magnesium, silver, sulphur, iron, oxygen, lead, chlorine, aluminum.

(*b*) Classify the following metals under the headings (*i*) Reduced by carbon or hydrogen, (*ii*) Not reduced by carbon or hydrogen: sodium, silver, copper, aluminum, magnesium, calcium, iron, lead, bismuth, mercury.

(*c*) Classify the metals in (*b*) above under the headings, (*i*) Attacked by water or dilute HCl, (*ii*) Attacked only by oxidizing acids.

(*d*) How can the acitivity series be used to predict the corrosion resistance of a combination of metals?

7. (*a*) How does a prospector know when he has found a valuable mineral?

(*b*) What would you do to find the density of a piece of granite?

(*c*) Calcite (calcium carbonate) looks very much like quartz (silicon dioxide). What field tests could you use to distinguish them?

(*d*) What is meant by blow-pipe analysis?

(*e*) What is meant by qualitative analysis?

(*f*) How is a complex mixture of metal ions separated into groups in qualitative analysis?

(*g*) Give the colour of the following sulphides and write *ins.* after the formula if it is not soluble in very dilute hydrochloric acid: As_2S_3, ZnS, PbS, FeS, CuS, Ag_2S, Sb_2S_3, Bi_2S_3.

(*h*) Why can Al_2S_3 not be prepared by precipitation from solution?

(*i*) Describe briefly how you would test the following compounds to show the presence of both the cation and the anion:
$(NH_4)_2SO_4$, $PbCO_3$, $AlCl_3$, $CuSO_3$, $Zn(NO_3)_2$, FeS, Na_3PO_4, KI, $Ca(OH)_2$, $BaBr_2$, Ag_2S.

Chapter 39

Getting Metals from Nature

1. Introduction. After a prospector or geologist finds a mineral or valuable compound of a metal the extent of the deposit is proved by drilling holes with diamond-edged drills and examining the cores which are brought to the surface. If it looks worth while a mine is dug with vertical shafts and lateral levels to permit the safe removal of the mineral and its surrounding *useless rock* or *gangue*. The *ores* are rocks containing minerals and they are brought to the surface by hoists which lift small cars. The process of getting the mineral and its adhering waste material to the surface is called *mining*.

After the rock or ore is mined it is usually crushed and as much as possible of the valuable mineral is collected together. This process is called *ore dressing* or *concentration*. The ore itself or the concentrated material is then treated to secure the metal in the condition required by the manufacturing industries. The process of extracting the metal and putting it into the required form is called *metallurgy* (see Fig. 209).

The exact nature of the processes used for mining, concentrating and extracting the metal depend upon the amount of mineral in the ore, its nature and the nature of the gangue. From the previous chapter you have learned that all the important minerals, except copper, silver, gold and the platinum metals which occur free, will be found as oxides, sulphides, carbonates, silicates, phosphates, sulphates and compounds of a few other non-metallic elements or radicals. Since oxygen is so active and abundant most elements occur

as single oxides or molecular compounds of metallic and non-metallic oxides. The next most abundant class is the sulphides, and these can be converted to oxides by heating in air since oxygen is more active as a non-metal than sulphur.

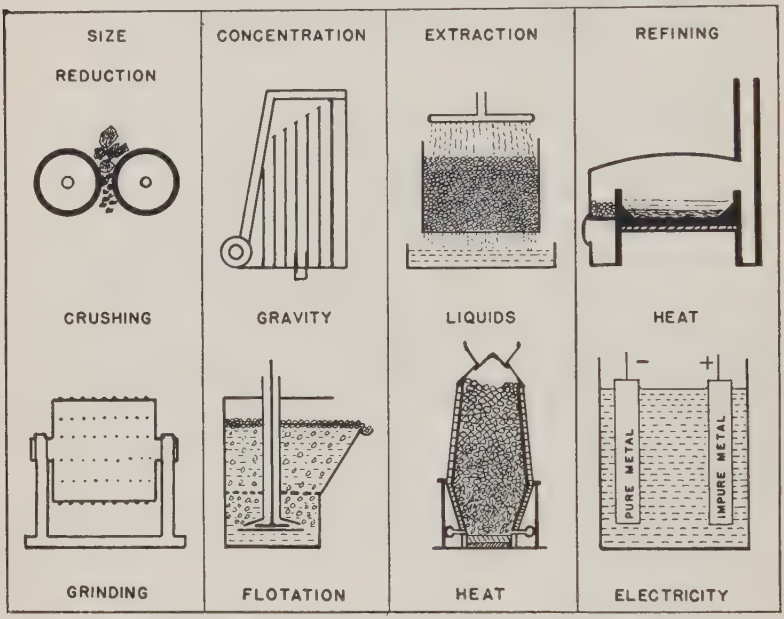


Fig. 209. Processes used in the extraction of metals from ores.

The heating of ores to produce a chemical change in them is called *roasting*. Where considerable amounts of heat are used in several complicated reactions to alter, concentrate or recover a metal or its compounds, the process is often called *smelting*. We thus speak of the copper smelters at Copper Cliff, Ontario; the zinc smelters at Flin Flon, Manitoba; or the lead smelters at Trail, B.C.

2. Concentration or ore-dressing. The ores containing minerals are practically never composed of only one mineral although some specimens of hematite are nearly pure iron oxide, Fe_2O_3. The ores containing the minerals are blasted

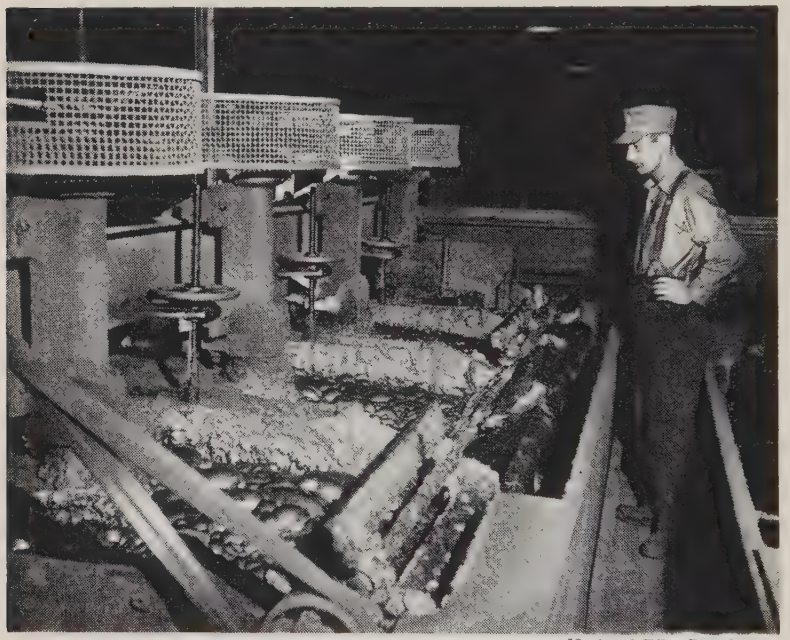
into large pieces with dynamite or other explosives before they are brought to the surface. Here they are crushed fine enough to free the valuable mineral from the worthless gangue. This may be done by various kinds of machinery such as jaw crushers, gyratory crushers, rolls, ball mills and many other special types. After the ore is crushed it is separated by either gravity separation or froth flotation.

Gravity separation processes depend on the different rates of sedimentation or settling which occur because of the difference in density between the mineral and the gangue. If two equal-sized particles of different densities are allowed to fall in a liquid the denser particle will settle more rapidly and if they are stirred up in the liquid the denser particles will not rise as far as those less dense. There are a large number of devices for making use of the differential rates of settling of the particles, and they depend mostly on shaking the material up in water in such a way as to allow the less dense material to overflow and the denser material to flow along a table or remain on a screen. A widely used device is a sloping table with riffles or ribs at right angles to the flow of water over it. It is given a shaking motion and the less dense material flows over the riffles while the denser material flows along the riffles to the end. The use of a pan to separate gold dust from sand by washing with water is a simple example of gravity separation. The gangue which overflows is known as *tailings*.

3. Froth flotation. The discovery of methods of altering the wettability of surfaces has revolutionized the mining of non-ferrous metals, especially in Canada. It has made it possible to work low-grade ore deposits profitably and even to rework the tailings of many gravity separation processes.

If a dense mineral such as zinc sulphide has a very thin film of oil on its surface and air is blown through the water in which it is sinking, tiny bubbles of air cling to the surface

of the mineral because the oily surface repels water and attracts air. These bubbles of air act as little floats to lift the mineral to the surface where it is skimmed off. Each flotation cell makes a partial separation and a battery of such cells will select zinc sulphide so perfectly that only a trace is left in the tailings or gangue. The process is illustrated in Fig. 210.



National Film Board photo

Fig. 210. Valuable zinc sulphide is floated away from the rock.

The process may also be used to separate one mineral from another. There are three classes of chemicals used in the process. The *frothers* such as pine oil, tar and creosote lower the surface tension of the water and allow a foam to be produced. The *promoters* form an almost monomolecular film on the surface of the particles and they are specially chosen so that one end of the molecule clings well to the

mineral and the other end presents a water-repellent surface. The chief promoters are organic compounds called *xanthates*. The *depressants* make the surfaces of other minerals or gangue particles more wettable by water. They are bases and cyanides which promote the wetting of silicate or oxide surfaces. By suitable choice of promoters and depressants almost any mixture of minerals may be separated.

4. Roasting. After the ore has been concentrated it may require conversion to another compound before the metal can be extracted. Sulphides and carbonates must be changed to oxides, oxides may be converted to soluble salts, and the water of hydration of salts is often removed. Sulphide ores are usually converted to oxides before extraction begins but carbonates may be heated to oxides at the same time as the extractive process is taking place.

In roasting, the sulphides are heated with air to allow the oxygen to convert them to the oxides. The relative stability of the various sulphides to oxidation makes it possible to oxidize them selectively by careful control of the time, temperature and the amount of air admitted to the mass. These operations are carried out in various ways. The oldest method was roasting in heaps with cordwood. The destruction of the surrounding vegetation and the inefficiency of the process have made it obsolete. Nowadays the sulphur is removed in ovens or furnaces. These may be *rotary ovens* through which the crushed ore slowly works its way in a stream of hot air, *reverberatory* furnaces with mechanical rakes, or *rotary furnaces* similar to a cement kiln. Some modern installations use a row of furnaces with a *travelling grate*.

5. Leaching. All minerals are not separated from the gangue by heat treatment, gravity separation or flotation. The concentrated pulp may be *extracted* with solvents. The noble metals such as gold and silver may be dissolved by

sodium cyanide because the complex ions of these metals are very stable.

$$4\,Au + 8\,NaCN + O_2 + 2\,H_2O \longrightarrow 4\,NaAu(CN)_2 + 4\,NaOH$$

They may also be dissolved by mercury and the process is called *amalgamating*. The pulp is agitated in a barrel with mercury, and the noble metals form an *amalgam* from which the mercury may be distilled, leaving the metal. Zinc and low-grade copper ores may be extracted with sulphuric acid and the metal recovered from the solution by electrolysis.

6. Reduction with carbon. Unless a metal occurs in the native state and is removed by amalgamation with mercury it is usually obtained in the form of a compound and must be reduced to the free metal by the chemical process known as reduction. There are three distinct types of procedure:

(1) Reduction with carbon.
(2) Reduction with metals.
(3) Reduction by electricity or electrolysis.

More tons of metal are produced by reduction with carbon than by any other method. Carbon in the form of *coke* is the reducing agent because it is efficient and can be made rather cheaply from soft coal. The process is carried on in blast furnaces similar to that described under the extraction of iron (Chap. 40). A *flux* is added with the coke and it combines with the gangue to form a *slag* or molten rock which floats on the metal to prevent its oxidation by the blast of air used to burn part of the coke. Only enough air is supplied to burn the coke to carbon monoxide so a reducing atmosphere is maintained. The flux used will be an acidic oxide if the impurity is a basic oxide such as lime or magnesia. Silica in the form of sand is a common acidic flux.

$$SiO_2 + CaO \longrightarrow CaSiO_3$$

Dolomitic limestone will be added if the impurity is mainly

quartz, which is a form of silica. The heat generated by the burning coke converts the carbonates to oxides which combine with silica.

$$CaCO_3 \longrightarrow CaO + CO_2$$

Since the slag is a molten rock it runs out like melted glass. The metal is also removed in the fluid state so that the operation is continuous.

7. Reduction with metals. (*i*) *Dry methods.* Aluminum oxide, magnesium oxide, and the oxides of the light metals which are near the top of the activity series are too stable to be reduced with carbon. They may be displaced from their oxides by heating with a more active metal whose oxide has a higher heat of formation. Since aluminum oxide (alumina) has a very high heat of formation and aluminum is a very active metal, it can be used to displace a great many metals from their salts or oxides. The reduction is accompanied by extremely high temperatures since

$$4\ Al + 3\ O_2 \longrightarrow 2\ Al_2O_3 + 685{,}200\ \text{calories}$$

A great many metal oxides and even some non-metal oxides can be reduced with aluminum (see Chap. 34, sec. 11).

(*ii*) *Wet methods.* Many minerals are recovered by leaching with cyanides, alkalis, or acids, and the metal may be thrown out of the solution by treatment with a metal which is higher in the activity series. This method is particularly useful in the recovery of the more valuable metals in waste solutions. Scrap iron may be used to recover copper from the wastes of the copper industries. Silver may be recovered from the wastes of the photographic industry by hanging zinc strips in the solutions.

8. Reduction by electricity—Electrometallurgy. The electric current may be used to provide two essentials of the reduction process:

(1) Heat for smelting or conversion.

(2) Cathodic reduction of the metal compound.

Since the cathode supplies electrons to the positive ions it exerts a reducing action of any desired magnitude by regulation of the applied voltage. You have seen that the activity series is associated with a list of potentials which must be exceeded before the ion may be reduced to the metal.

Many types of equipment are needed for the diverse applications of electricity in the separation and purification of metals.

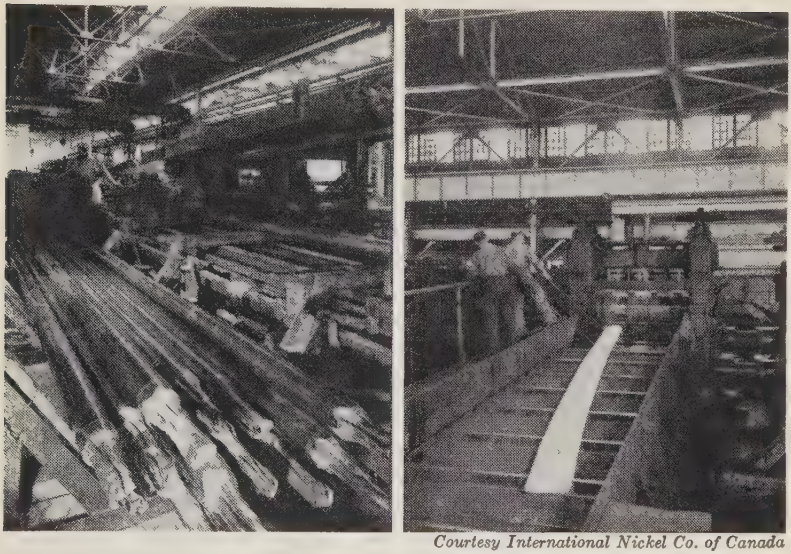
(1) *Furnaces* use the heat of the current for smelting and fluxing as well as the electrolytic effect for the separation of the metal.

(2) *Cells* use the electrolysis effect for the separation or purification of metals. This is often called electrolytic refining.

Courtesy Consolidated Mining and Smelting Co.

Fig. 211. Lead is separated electrolytically from silver, gold, antimony and bismuth in these Betts cells.

Electric furnaces may be *direct arc*, *radiation arc* or *induction furnaces*. They are used mostly for the production of special steels. Electrolysis cells are used when oxides and salts cannot be reduced with some cheap reducing agent like carbon.



Courtesy International Nickel Co. of Canada

Fig. 212. Fabricating tubing by cold drawing (left) and hot rolling bars on a 24-inch mill (right).

9. Fabricating. The pure metal or a mixture of metals which is suitable for industrial use is subjected to forming processes. The metal is often remelted in a cupola, reverberatory or electric furnace and the correct amount of alloying element added. It is then poured into ingots which can be forged, rolled, extruded or drawn into the required shape. Often the alloy is cast directly into the rough form of the finished product and later machined. The cooling and annealing of the metal are very important in determining the nature of the crystals in its structure and hence its physical properties.

The operation of remelting is similar to the operations in smelting and refining. The processes of fabrication involve mainly physical changes which can only be mentioned here.

Question Summary

1. Define the following terms: ore, gangue, mineral, mining, ore dressing, metallurgy, roasting, smelting.

2. (*a*) Give the geological names for the following minerals: PbS, Al_2O_3, Fe_2O_3, ZnS.

(*b*) State the principle of gravity separation devices.

3. What is the function of each of the following in froth flotation: air, frothers, promoters, depressants?

4. (*a*) Write balanced equations for the roasting of: FeS, Cu_2S, ZnS, $FeCO_3$, and Ag_2S.

(*b*) Name four types of equipment used for roasting ores.

5. Describe briefly with examples two methods of leaching ores.

6. (*a*) Enumerate three types of reduction process and give an example of each.

(*b*) Explain the function of each of the following in the blast furnace process: coke, flux, slag, air. Illustrate your answer with equations.

7. (*a*) Explain with a few examples why aluminum may be used to reduce metallic oxides.

(*b*) To the sulphates of bismuth, copper, cadmium and antimony in solution metallic zinc is added. Write equations for the reactions which occur.

8. (*a*) In the electrolysis of aluminum, what metals would have to be previously removed in order to keep them from contaminating the metal? What metals could be left in the bath?

(*b*) Describe some of the types of equipment used in the reduction of compounds by electricity.

(*c*) How are metals purified by electrolysis?

9. Mention briefly the processes of fabrication.

Chapter **40**

The Iron and Platinum Metals

1. Introduction. Each of the long periods of the periodic table contains three transition elements which are placed in Group VIII. They all have incomplete inner shells of electrons. These elements are grouped into three triads:

1. Iron, cobalt and nickel.
2. Ruthenium, rhodium and palladium.
3. Osmium, iridium and platinum.

All these elements are metals and form compounds with positive valences of 2 and 3. The metals of the first triad are more abundant and of greater importance than those of the second and third triads. Iron, cobalt and nickel resemble one another and are active metals, while the others are noble metals, of which platinum is the best known.

IRON

2. History and occurrence. Iron has been used by man for many years, and iron implements which are probably five thousand years old have been found in Egypt. The early method of obtaining the metal was to mix iron ores with charcoal and cover the mass with a layer of clay, leaving holes at the top and bottom of the heap to produce a draught. The charcoal was then ignited and the ores were reduced by the carbon and by the carbon monoxide which was produced. The use of the blast furnace was a considerable improvement and large-scale production of iron commenced early in the seventeenth century when coal was used to reduce the ores. Coke has been used in the preparation of iron since the beginning of the eighteenth century.

Small amounts of iron are found free in the earth, and most meteorites are composed of the free metal. Iron occurs chiefly as the oxides, *hematite*, Fe_2O_3, *limonite*, $2Fe_2O_3.3H_2O$ and *magnetite*, Fe_2O_3; the carbonate, *siderite*, $FeCO_3$; and the sulphide, *pyrite*, FeS_2. The most important ore is hematite. Pyrite is usually used as a source of sulphur and not of iron. The iron ores are abundant and contain large percentages of iron. The United States produces about one-half of the world's supply, the other principal iron-producing countries being France, Germany, Great Britain, the U.S.S.R., Sweden and Canada. The greater part of the ore smelted in Canada comes from Newfoundland and the region around Lake Superior. A large new body of iron ore has been found near the Quebec-Labrador border. The Great Lakes provide the waterway for the ore to the blast furnaces at Sault Ste. Marie and Hamilton, Ontario, and the Newfoundland ore is smelted at Sydney, Nova Scotia. The raw materials for the production of iron consist of ore, coke and limestone, and the furnace must be located near the source of these materials to ensure economic operation. Iron compounds are found in almost all rocks and soils, to which they add a red or brown colour. Iron is present in the chlorophyll of green plants and in the haemoglobin of the blood.

3. The blast furnace. The blast furnace in which the iron ores are reduced consists of a vertical steel tower lined with fire-brick. It is about 95 feet in height and about 28 feet in diameter at the widest part which is about one-third of the way up. A blast furnace is shown in Fig. 213. The furnace tapers towards the top and bottom. At the top is a trap, called the *bell*, through which the carefully weighed charge of ore, limestone and coke is fed. Immediately below the widest part of the furnace there is a constriction called the *bosh* which acts as a support for the charge. The bottom of the furnace is known as the *crucible*. Just above the crucible

preheated air is blown into the furnace through pipes called *tuyeres* (twers). *Blast furnace gas*, which is produced during the operation of the furnace, is led off through pipes at the top.

The coke is added to provide fuel for the process and to act as a reducing agent, either by itself or by the production of carbon monoxide. Most iron ores contain silica which must

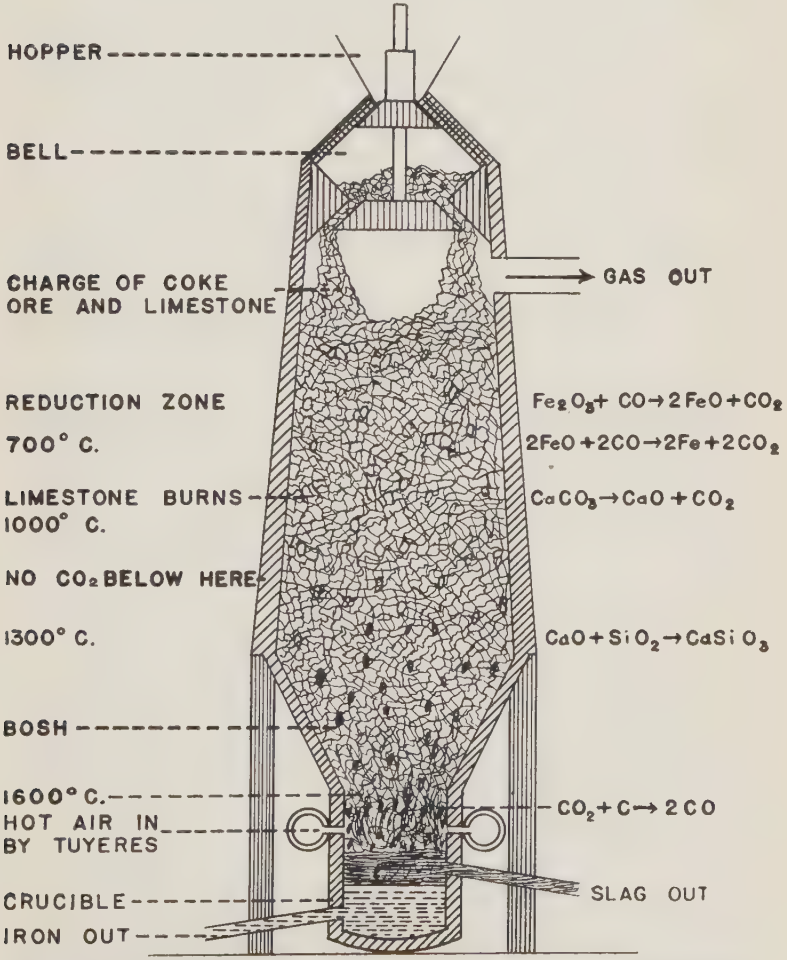


Fig. 213. The parts, conditions and reactions in an iron blast furnace.

be removed. The addition of limestone causes the formation of a fusible mass of silicates and aluminates known as *slag* which collects in the crucible on top of the molten iron. If the iron ore contained lime, silica would be added to form the slag. The slag is a necessary part of the process since it protects the iron from oxidation, which would be rapid at the high temperature of the bottom of the furnace, and it allows the drops of liquid iron to collect into a single mass. The slag is drawn off from time to time and may be used in the manufacture of cement, for liming soils, and as railroad ballast, although it is frequently discarded. The dumping of the molten slag is an interesting part of the process to watch, especially during the night. The molten iron is removed from the crucible about every six hours, and the operation of the furnace is continuous. The blast furnace gas, which consists chiefly of carbon monoxide and nitrogen, may be burned to heat the air which is fed to the furnace, or it may be used to operate engines or boilers around the plant.

The operation of the blast furnace may be explained by the following simplified reactions. The air which enters the furnace burns some of the coke to carbon dioxide at a temperature of about 1600°C. It is immediately reduced to carbon monoxide as soon as it encounters any excess coke.

$$CO_2 + C \rightleftarrows 2\ CO$$

This reaction runs to completion to the right at temperatures above 1000°C. so there is plenty of carbon monoxide in the furnace. Above the top of the bosh the limestone is decomposed wherever the temperature exceeds 800°C. to form calcium oxide and carbon dioxide.

$$CaCO_3 \longrightarrow CaO + CO_2$$

The silica in the ore reacts with the calcium oxide to form the slag which consists chiefly of calcium silicates and runs

to the bottom of the furnace whence it is drawn off as described.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

The carbon dioxide produced passes up through the heated material and is reduced to carbon monoxide by the hot carbon. The carbon monoxide then acts as a reducing agent. About 20 feet below the top of the furnace, where the temperature is around 600°C. the ore is reduced to ferrous oxide by the carbon monoxide.

$$Fe_2O_3 + CO \longrightarrow 2\ FeO + CO_2$$

As the charge moves downward the ferrous oxide reaches the lower portions of the furnace where the temperature is around 800°C. and is reduced to metallic iron.

$$2\ FeO + 2\ CO \longrightarrow 2\ Fe + 2\ CO_2$$

The temperature of the furnace at the hottest point near the tuyeres may reach over 1800°C. but the iron produced in the furnace usually melts between 1150°C., and 1250°C. because of the impurities present.

The iron which is run off from the furnace may be taken to a steel mill in large buckets, but much of it is cast into forms known as *pigs*. These forms received their name since the shape of the moulds bore a marked resemblance to suckling pigs. Pig iron contains from 2 to 5 per cent of carbon and small amounts of sulphur, manganese and phosphorus. It has a low tensile strength and is very brittle. One furnace will produce from 600 to 1200 tons of pig iron every 24 hours.

4. Cast Iron. When pig iron is melted, run into moulds, and allowed to cool, *cast iron* is produced. If the molten iron is allowed to cool slowly, the carbon in the iron will be present in the form of large flakes of graphite and the product is known as *grey cast iron.* It has a low tensile strength and

cannot be rolled, welded or forged. It is used to make articles which may be cast and do not need machining, such as radiators and stove parts. If the molten pig iron is cooled suddenly in the moulds, *white cast iron* is produced. In this variety of iron, the carbon is present largely as the carbide, *cementite*, Fe_3C. It is very hard and brittle. If white cast iron is heated for several hours at a red heat and then allowed to cool slowly, *malleable cast iron* is produced. In malleable castings the carbon is present in the form of small pieces of graphite. This variety of cast iron is not as strong as steel, but the castings are easy to make and are cheaper. They are used for parts of machinery and for locomotives.

5. Wrought iron is made by heating pig iron with iron oxide in a reverberatory furnace. This type of furnace is shown in Fig. 214. The charge consists of a layer of iron

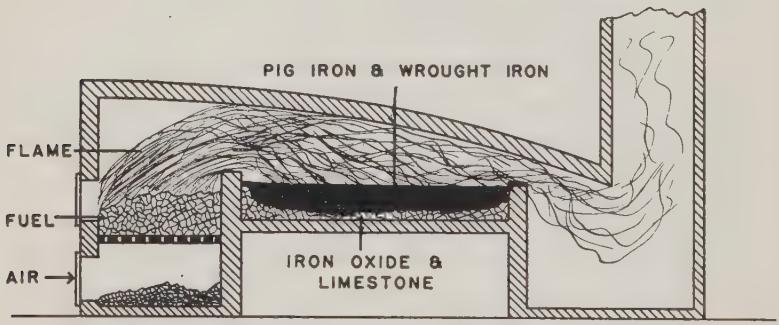


Fig. 214. Reverberatory furnace in which impurities are removed from cast iron by heating it with iron oxide.

oxide with pig iron on top. The flames and hot gases from the fire are reflected from the roof of the furnace to the charge. When the iron melts, the impurities are oxidized by the iron oxide. Carbon and sulphur are converted to their oxides which pass out as gases. Phosphorus and silicon are converted to oxides which form a slag with the iron oxide or limestone which are added as required. The iron from

which these impurities have been removed has a higher melting point than pig iron and it commences to harden. The charge is then worked, or *puddled*, by iron rods and removed from the furnace in the form of large balls called *blooms*. These balls are hammered or rolled to remove the slag. Wrought iron is very pure iron containing about 0.2 per cent of carbon. It is softer and stronger than cast iron but not as strong as steel. It is malleable and ductile, and it is used to make articles which are hammered into shape while hot, such as horseshoes, anchors and ploughshares, and for making wire. Since it is less fusible than cast iron it is used for stove grates.

6. Steel. Steel is a variety of iron which is richer in carbon than wrought iron, but almost free from sulphur, phosphorus and silicon. It is produced from pig iron by burning out the impurities and then adding various metals, such as tungsten, nickel, chromium and manganese, depending upon the specific properties desired. Steel combines the properties of wrought and cast iron since it is elastic and hard, but it may be forged and welded. It has a greater tensile strength than wrought iron, it can be tempered, and it can be magnetized permanently. The two most common methods of making steel are the *Bessemer* and the *Open Hearth* process.

A. The Bessemer process.

In this process, which was developed by Bessemer in 1856, the impurities are burned out of the iron by a blast of air. The molten iron is placed in an egg-shaped vessel known as a *converter*, and a blast of air is blown through holes in the bottom. The converter is made of steel lined with fire-brick and holds from 15 to 25 tons of steel. The fire-brick lining is usually silica brick, which unites with the basic oxides of the impurities. This *acid* lining does not unite with the oxides of phosphorus or sulphur, so that if the pig iron contains large amounts of these elements a *basic* lining made of

dolomite is used. The converter, which is shown in Figs. 215 and 216, is mounted on trunnions so that it may be tipped to deliver its charge. When the air is forced into the converter the impurities are oxidized and flames and sparks are shot out of the mouth with a dazzling brilliance. The blast is continued for 10 to 20 minutes until the appearance of the flame tells the experienced operator that the impurities are oxidized. The remaining impurities form a slag; this floats on the top of the liquid which is almost pure iron. The quantities of the metals required to produce the kind of steel desired are then added. Some oxygen will remain in the steel and to remove it materials known as *deoxidizers* are added. If the oxygen were not removed it would form small bubbles which would weaken the finished steel. The converter is tilted and the charge poured into moulds to cool. The resulting ingots are then rolled or hammered into various shapes as desired. Steel produced by the Bessemer process is considered to be inferior to that made by the open hearth process, since it is more likely to contain flaws. The process is more difficult to control since it must be carried out rapidly. The air blast cannot be left on too long or the iron will oxidize, and the charge must be poured quickly before it solidifies. Bessemer steel contains from 0.1 to 1.0 per cent of carbon and is used to make rails and structural steel. It is cheaper than steel made by the open hearth process but the rigid specifications of modern technology have made the Bessemer process less desirable.

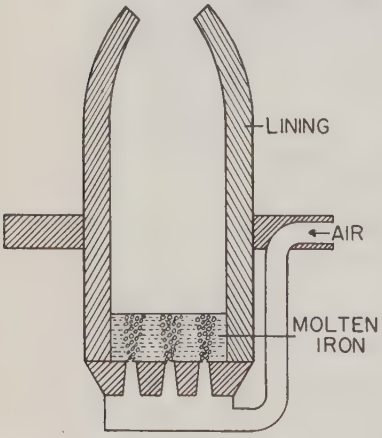


Fig. 215. Impurities may be burned out of molten iron or nickel in a Bessemer converter.

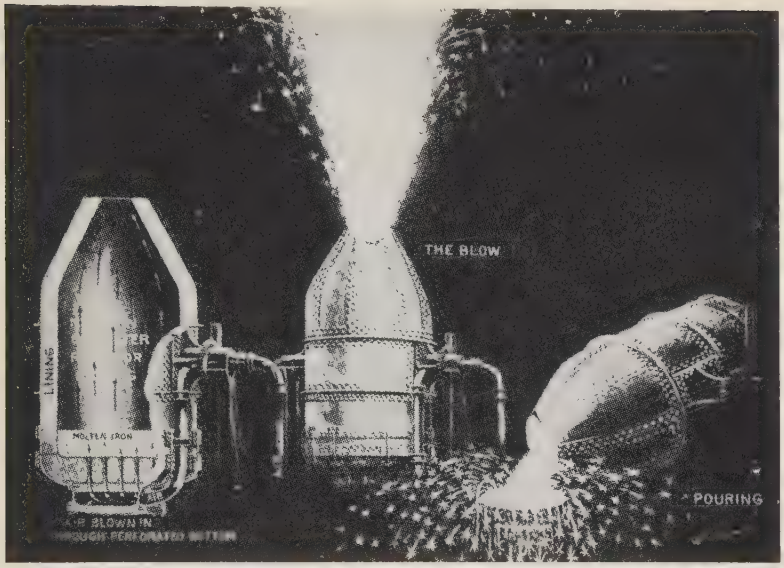


Fig. 216. Bessemer converter in action.

B. The open hearth process.

This process was developed by Siemens and Martin in 1863-1864. Cast iron is melted with steel scrap and iron oxide in a furnace which is shown in Fig. 217. The saucer-

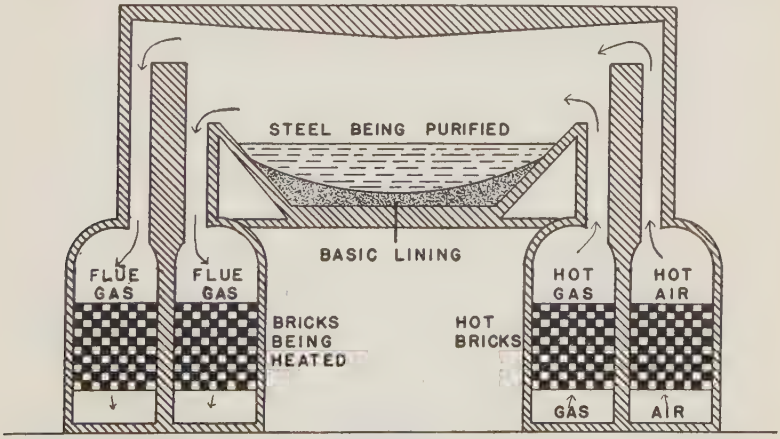


Fig. 217. Cast iron may be purified in a regenerative open hearth furnace.

shaped floor is lined with silica for the acid process, and with dolomite for the basic process. The acid process is used with iron which contains only small amounts of phosphorus. The furnace is heated with gas or oil and air which burn together over the iron. The gases pass over a preheater made of checkered brickwork on their way from the furnace, and after a time the gas flow is reversed so that the incoming gases pass through the heated checker-work, while the hot flue gases pass through a second preheater. The process is similar to the Bessemer as carbon is removed with the air as carbon dioxide and the other impurities are converted into a slag. Deoxidizers are added near the end of the reaction to remove the oxygen, and just before the charge is poured the required amounts of other metals are added. Open hearth steel is uniform in structure and more free from flaws than Bessemer steel. It is used for rails, armour-plate and for purposes where the metal is subject to considerable vibration. Since the open hearth process is slower than the Bessemer, it is possible to take samples of the steel from time to time and to stop the operation when the desired carbon content has been reached.

C. Crucible steel.

Crucible steel is a high-grade product which is made by heating steel from either the Bessemer or the open hearth process in the large crucibles of an electric furnace. The required amounts of the other elements are added and allowed to form an alloy with the iron. Since relatively small amounts are prepared at one time, the composition can be controlled carefully, and the steel has a uniform high quality. Crucible steel is used in the manufacture of razor blades, cutlery, springs, needles and similar articles.

7. Tempering. When red-hot steel is cooled slowly it is fairly soft, but if it is cooled quickly it becomes very hard. If the hardened steel is heated carefully, any degree of hard-

ness may be obtained. This treatment is known as *tempering*. The properties of steel depend a great deal upon the crystal state of the iron and the condition of the carbon. At temperatures up to 900°C. the iron is soft and is known as *alpha iron*. From 900°C. to 1400°C. the iron is harder and is known as gamma iron. Between 1400°C. and the melting point of about 1535°C. the iron is known as *delta* iron. In alpha iron dissolved carbon is deposited as particles of graphite, which make the iron soft and give it considerable tensile strength. In gamma iron the carbon is in the form of the carbide, *cementite*, and if this modification of iron is cooled rapidly the composition will not change, and a solid solution of cementite and gamma iron will result. This solid solution is known as *austenite* and is hard and brittle. If austenite be reheated to temperatures between 200°C. and 300°C. the composition will be changed, as the solid solution of cementite and iron will be broken up to some extent and the properties of the steel will be changed. By varying the length of time of heating, the temperature, and the rate of cooling, steels of varying degrees of hardness may be produced.

If low-carbon steel is heated in closed containers with powdered carbon and later quenched in oil, *case-hardened steel* is produced. The steel takes up some of the carbon in its surface layers, and forms a metal which has a long-wearing surface and a strong flexible core. This type of steel is used to make axles, wheels and articles which must show a resistance to wear, and at the same time must be sufficiently flexible to withstand sudden strains.

8. Alloy steels. In the manufacture of steel small amounts of other elements are added to the iron to act as purifiers. These substances insure the complete reduction of any iron oxide which may be present. Aluminum, manganese, silicon and titanium are often used for this purpose. The compounds formed by the oxidation of these elements are

removed in the slag and none of them remain in the finished product.

Other elements are added to steel to give it certain desirable properties. These elements, usually metals, dissolve in the molten steel and produce an alloy as the finished product. By varying the element and the amount of it that is present,

TABLE 41—ALLOY STEELS

Element	*Percentage*	*Property*	*Uses*
Cerium	70	Gives off sparks when scratched	Lighter flints
Chromium	1-5	Hard, strong, tough	Shafts and gears
	10-15	Resists corrosion	Stainless steel
Manganese	10-14	Hard, strong, tough resistant to wear	Teeth for steam shovels and rock crushers
Molybdenum	6-7	Holds temper when heated	High-speed tools
Nickel	2-4	Strong, tough, resists corrosion	Gun forgings, auto parts
	38 (Invar)	Low coefficient of expansion	Watches, measuring tapes
	78 (Permalloy)	High magnetic permeability	Electrical instruments
Nickel-chromium	8-20 Ni. 14-20 Cr.	Hard, strong, tough, resists corrosion	Stainless steel
Nickel-manganese	10-15 Ni. 5-10 Mn. (Nomag)	Practically non-magnetic	Electrical instruments
Silicon	1-2	Hard and strong	
	12-15 (Duriron)	Resists corrosive action of acids	Vessels for industries using strong acids
Tungsten	4-18	Holds temper when heated	High-speed cutting tools
Vanadium	0.1	Very hard	

a steel of almost any desired property may be produced. A list of some of the important alloy steels are given in Table 41.

9. The properties of iron.

(*i*) *Physical.* Pure iron is not prepared on a commercial scale. It may be made in the laboratory by electrolysis of ferrous sulphate solution, or by reducing pure ferric oxide by hydrogen. It has a silvery-white lustre, is ductile, malleable and relatively soft. Wrought iron is the purest form of iron which is prepared commercially. Pure iron melts at about 1535°C., wrought iron at about 1500°C. and pig iron at 1200°C.

(*ii*) *Chemical.* The most familiar chemical property of iron is *rusting.* Pure iron does not rust in cold water, but ordinary iron rusts in water or in moist air when oxygen and carbon dioxide are available. Rust is a porous coating of variable composition which does not adhere to the metal. It is chiefly a hydrated ferric oxide, $3Fe_2O_3.H_2O$. It is believed that ferrous bicarbonate is first formed by the carbon dioxide in the water.

$$2\ Fe + 4\ H_2CO_3 \longrightarrow 2\ Fe(HCO_3)_2 + 2\ H_2$$

The oxygen of the air then oxidizes it to hydrated ferric oxide.

$$12\ Fe(HCO_3)_2 + 3\ O_2 \longrightarrow 2\ (3Fe_2O_3.H_2O) + 10\ H_2O + 24\ CO_2$$

Iron is a relatively *active metal* as is shown by its direct combination with sulphur and chlorine, the burning of finely divided iron in air and the displacement of hydrogen from hydrochloric and sulphuric acids.

$$Fe + S \longrightarrow FeS$$

$$3\ Fe + 2\ O_2 \longrightarrow Fe_3O_4\ (Fe_2O_3.FeO)$$

$$2\ Fe + 3\ Cl_2 \longrightarrow 2\ FeCl_3$$

$$3\ Fe + 4\ H_2O \longrightarrow Fe_3O_4 + 4\ H_2$$

$$Fe + 2\,HCl \longrightarrow FeCl_2 + H_2$$
$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

Iron is a transition element and thus has a *variable valence.* Either two or three electrons are found in the valence shell and this gives rise to *two series of compounds.* The *ferrous* compounds are formed with *divalent* iron and the *ferric* compounds with the *trivalent* state. The ferrous and ferric salts have no resemblance to one another but are similar to other divalent and trivalent metal salts respectively. The ferrous salts are easily oxidized to the ferric salts by atmospheric oxygen or chlorine. By using cold dilute nitric acid it is possible to get ferrous nitrate but no hydrogen is evolved. The nitric acid is reduced to ammonia which unites with the excess nitric acid to form ammonium nitrate.

$$4\,Fe + 10\,HNO_3 \longrightarrow 4\,Fe(NO_3)_2 + 3\,H_2O + NH_4NO_3$$

When iron is dipped in concentrated nitric acid it forms a passive state in which it does not react with dilute acids. Passive iron becomes active again when scratched or struck. The formation of a passive state is also a property of chromium, cobalt and some other metals. An impervious and insoluble oxide film is formed.

10. Ferrous compounds. Ferrous salts are usually white when anhydrous and blue-green or green when hydrated. They give water a bitter taste, e.g., chalybeate water, and are easily oxidized to the ferric state so they are never pure if exposed to moist air.

Ferrous oxide, FeO, is a black powder which can be made by reducing ferric oxide with hydrogen or by the decomposition of ferrous oxalate. On exposure to the air it turns to ferric oxide.

Ferrous hydroxide, $Fe(OH)_2$, is thrown down as a whitish precipitate by the addition of a soluble hydroxide to a solu-

tion of a ferrous salt. On standing it becomes green and finally turns brown as it becomes oxidized to ferric hydroxide.

Ferrous chloride, $FeCl_2$, may be prepared by dissolving iron in dilute hydrochloric acid. The salt crystallizes from solution as the pale blue hydrate, $FeCl_2.H_2O$, which turns green on exposure to the air. It is used as a reducing agent and the action can easily be demonstrated by bubbling chlorine into the solution. The chlorine is all absorbed and the green solution turns orange as ferric chloride is formed.

$$2\ FeCl_2 + Cl_2 \longrightarrow 2\ FeCl_3$$

In this reaction the iron is oxidized from a valence of 2 to a valence of 3 by the loss of one electron from each ferrous ion while each chlorine atom is reduced from a valence of 0 to a valence of 1 negative by the gain of the electron. Oxygen will oxidize the ferrous salt in the same manner but the equation for the reaction is more complicated.

Ferrous sulphate, $FeSO_4$, may be prepared by dissolving iron in sulphuric acid and evaporating the solution. It crystallizes from solution as the hydrate, $FeSO_4.7H_2O$, which is known as *green vitriol* or *copperas*, and which is the most widely used ferrous salt. It is used in medicine as a disinfectant, also as a weed killer, wood preservative, reducing agent and in the manufacture of writing ink.

Writing ink is usually made by the addition of ferrous sulphate to tannic acid which forms ferrous tannate. Ferrous tannate is colourless, but it is oxidized by air to form black ferric tannate. This oxidation is prevented by the addition of sulphuric acid and a protective colloid like gum arabic. A blue dye is added to provide a colour when the ink is first used for writing. After the writing has stood for some time oxidation takes place and the black ferric tannate is formed. This is why most writing inks are known as blue-black; they will write blue and dry black.

Ferrous sulphide, FeS, is a black metallic-looking substance which may be prepared by direct combination of the elements. It may be precipitated by hydrogen sulphide from an alkaline solution of a ferrous salt. It is used in the preparation of hydrogen sulphide.

Ferrous carbonate, $FeCO_3$, is found in nature as the mineral *siderite*. It may be precipitated from solutions of ferrous salts by the addition of soluble carbonates. Like calcium carbonate, it is soluble in water containing dissolved carbon dioxide because of the formation of the bicarbonate, $Fe(HCO_3)_2$. *Chalybeate water* is a natural water containing ferrous bicarbonate in solution.

11. Ferric compounds. These are white when dehydrated and yellow, orange or brown when hydrated or in solution. The salts are much less metallic than the ferrous salts and are strongly hydrolyzed in solution because of the insolubility of ferric hydroxide. The carbonates and sulphides are completely hydrolyzed in water so they do not exist in neutral solutions. A good example of hydrolysis is ferric acetate which gives a red-brown precipitate of basic ferric acetate and a strong odour of vinegar when dissolved in water and heated.

$$\mathbf{Fe(C_2H_3O_2)_3 + 2\ H_2O \longrightarrow Fe(OH)_2C_2H_3O_2 + 2\ HC_2H_3O_2}$$

Ferric salts are oxidizing agents as they are easily reduced to the ferrous condition by nascent hydrogen, sulphur dioxide, potassium iodide and stannous chloride. For example, if a piece of zinc or iron is placed in an acid solution of ferric chloride or ferric nitrate lightly stoppered to prevent the re-entry of oxygen, the ferric ions are all reduced to ferrous ions.

$$\mathbf{2\ Fe(NO_3)_3 + H_2 \longrightarrow 2\ Fe(NO_3)_2 + 2\ HNO_3}$$

Sulphur dioxide can be used to reduce any ferric salt but the equations are awkward to write unless ferric sulphate is considered.

$$Fe_2(SO_4)_3 + SO_2 + 2\ H_2O \longrightarrow 2\ FeSO_4 + 2\ H_2SO_4$$

Stannous chloride is commonly used to reduce ferric chloride solutions.

$$2\ FeCl_3 + SnCl_2 \longrightarrow 2\ FeCl_2 + SnCl_4$$

Ferric oxide, Fe_2O_3, is an insoluble red powder which may be obtained by roasting pyrite or by igniting ferric hydroxide. It occurs in nature as the iron ore *hematite*. Pure ferric oxide is used commercially as *jeweller's rouge* and *Venetian red*. The latter is used as a pigment in paints for barns and structural ironwork. The mineral *magnetite*, Fe_3O_4, is a combination of the two oxides of iron and its composition may be represented as $FeO.Fe_2O_3$. This oxide is formed when iron is heated in air and is known as *hammer scale*, since it is produced when a blacksmith hammers iron. When iron is heated in air the oxide forms a durable scale on the surface and prevents further oxidation. This type of surface is known as *Russia iron* and is used in gun barrels.

Ferric oxide may be dissolved in dilute acids to give ferric salt solutions. The "pickling" of iron is the removal of the oxide by acids usually hydrochloric or sulphuric acid.

$$Fe_2O_3 + 6\ HCl \longrightarrow 2\ FeCl_3 + 3\ H_2O$$
$$Fe_2O_3 + 3\ H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 3\ H_2O$$

Ferric hydroxide, $Fe(OH)_3$, is precipitated as a reddish gel from solutions of ferric salts by the addition of a soluble hydroxide. It is usually considered to be ferric hydroxide, but it may be a mixture of hydrated ferric oxides.

$$FeCl_3 + 3\ KOH \longrightarrow 3\ KCl + Fe(OH)_3$$

It dissolves in acids to form ferric salts.

$$Fe(OH)_3 + 3\ HCl \longrightarrow 3\ H_2O + FeCl_3$$

Ferric chloride, $FeCl_3$, may be prepared by passing chlorine over iron, or by the addition of hydrochloric acid to ferric

hydroxide. The anhydrous salt forms black crystals, but the most familiar form of the salt is the yellow hexahydrate, $FeCl_3.6H_2O$. The salt is used in medicine as *tincture of iron*, when it is dissolved in an alcohol-water mixture. It is used as a chemical reagent in analysis and as a mordant in dyeing.

Ferric sulphate, $Fe_2(SO_4)_3$, is obtained by oxidizing ferrous sulphate. It may be evaporated from solution as a white mass but it does not form crystals. It forms alums with other salts, as *ferric ammonium alum*, $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$, and *iron alum*, $K_2SO_4.Fe_2(SO_4)_3.24H_2O$, which are used as oxidizing agents in chemical analysis. These alums do not contain aluminum but they are of the alum type, hence their name (see Chap. 34, sec. 14).

12. The iron cyanides. When potassium cyanide is added to solutions of ferrous or ferric salts, the iron cyanide produced reacts with an excess of potassium cyanide to form complex cyanides of potassium. These salts are known as *potassium ferrocyanide* and *potassium ferricyanide*.

Potassium ferrocyanide, $K_4Fe(CN)_6.3H_2O$, known as *yellow prussiate of potash*, is made by heating animal refuse, such as blood, with potassium carbonate and iron filings. After heating, the product contains potassium cyanide and ferrous sulphide, which interact in the presence of water as follows:

$$2\ KCN + FeS \longrightarrow Fe(CN)_2 + K_2S$$
$$4\ KCN + Fe(CN)_2 \longrightarrow K_4Fe(CN)_6$$

The trihydrate mentioned above crystallizes from water in large yellow crystals. The solution may be used as a test for the ferric ion, since with ferric salts a gelatinous precipitate known as *Prussian blue* is formed.

$$4\ FeCl_3 + 3\ K_4Fe(CN)_6 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12\ KCl$$

Prussian blue is *ferric ferrocyanide*. It is used to make laundry blueing which is used to correct the yellowish tint caused by ferrous bicarbonate in water.

Potassium ferricyanide, $K_3Fe(CN)_6$, which crystallizes from solution as red crystals, may be made by oxidizing potassium ferrocyanide with chlorine. It is used as a test for ferrous salts. With ferric salts it forms a brown solution, but with ferrous salts it produces a deep blue precipitate of *ferrous ferricyanide* or *Turnbull's blue*.

$$3\ FeCl_2 + 2\ K_3Fe(CN)_6 \longrightarrow Fe_3[Fe(CN)_6]_2 + 6\ KCl$$

Potassium thiocyanate, KCNS is also used to distinguish ferrous from ferric salts in solution. With ferric salts the thiocyanate produces a blood-red coloration.

13. Blueprints. Blueprint paper is prepared by dipping the paper in a solution containing potassium ferricyanide and ferric ammonium citrate, and allowing it to dry in the dark. To make the print, the paper is placed behind the drawing in a frame, and exposed to sunlight. The action of the light reduces the ferric compound to the ferrous in places where the blueprint paper is not protected by the black lines of the drawing. After exposure, the print is placed in water. The potassium ferricyanide reacts with the ferrous salt to form the insoluble Turnbull's blue. The ferric salt will not be acted upon, and will be washed away in the water. The result is the familiar blueprint, where the surface of the paper is blue and the lines of the drawing are white.

COBALT

14. Occurrence. In olden times ores of nickel and cobalt were mistaken for those of copper. Failure to obtain copper from these ores was ascribed to the presence of evil spirits and the word *cobalt* is said to be derived from the German "*Kobald*", an evil spirit. The metal was isolated by Brandt in 1735. Cobalt occurs as *cobaltite*, CoAsS, *smaltite*, $CoAs_2$, and *linnalite*, Co_3S_4. Large deposits of these minerals are found in Ontario, in conjunction with silver ores.

15. Properties and uses. Cobalt is a silver-grey, ductile, malleable, and magnetic metal. It combines with oxygen to form the oxide, Co_3O_4, which is analogous to Fe_3O_4, being a compound oxide, $CoO.Co_2O_3$. It combines directly with the halogens, sulphur, and carbon. It displaces hydrogen slowly from dilute acids.

Cobalt is used in making alloys such as *stellite*, an alloy containing cobalt, iron and varying amounts of other metals. This alloy is used to make high-speed cutting tools and surgical instruments. Crystals of tungsten carbide embedded in cobalt form a substance known by the trade name of *carboloy* which is used to make cutting tools.

16. Compounds of cobalt. Cobalt compounds are much like iron compounds with the exception that they dissolve in ammonia. Cobalt shows valences of 2 and 3, but the cobaltous compounds are the most common. The cobaltic salts are not very stable.

NICKEL

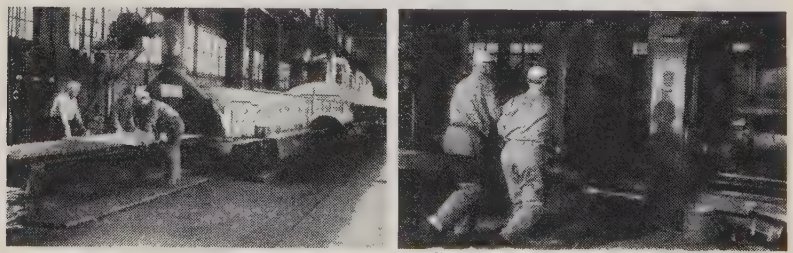
17. Occurrence and metallurgy. As in the case of cobalt, nickel ores were mistaken for those of copper, and when copper could not be obtained, these ores were given the name of *kupfernickel*, where "kupfer" indicated the copper, and "nickel" the devil which prevented the extraction of the desired metal. Nickel was obtained by Cronstedt in 1754.

Nickel occurs as *pyrrhotite*, a mixture of the sulphides of nickel, copper and iron; and in *garnierite*, a silicate of nickel and magnesium. The metal is also found with iron in meteorites. The largest part of the world's supply is obtained from the pyrrhotite deposits in Ontario.

The ores are smelted in a blast furnace to yield a *matte* of the sulphides of nickel and the other metals. Mixture of the matte with silica and treatment in a converter oxidizes the iron and converts it to slag.

Further heating of the matte oxidizes the nickel sulphide to the oxide, which is reduced by carbon. In the *Mond process*, the oxides of nickel, copper and cobalt are heated in a stream of water gas. The oxides are reduced and the nickel combines with the carbon monoxide to form a gas, *nickel carbonyl*, $Ni(CO)_4$, which is very poisonous. When this gas is heated to about 200°C. it decomposes into nickel and carbon monoxide. Very pure nickel is obtained by this process.

18. Properties and uses. Nickel is a silvery hard metal which is highly resistant to corrosion and is fabricated like steel. It is not attacked by air under ordinary conditions, but finely divided nickel will ignite spontaneously to form the monoxide. It resembles cobalt and iron but it is less active towards dilute acids and steam. It dissolves in dilute nitric acid, and is rendered passive by concentrated nitric acid.



Courtesy International Nickel Co. of Canada

Fig. 218. Annealing furnace for Monel sheet (left) and hot rolling of sheet (right).

Nickel is used in alloys, in alloy steel and in nickel plating. Some of the important alloy steels containing nickel have been listed in Table 41. *Monel metal* is about one-third iron and copper and two-thirds nickel, and is an important metal which is often used as a covering for sinks and soda fountains. *German silver* is an alloy of nickel, copper and zinc (1:2:1). Nickel coinage in Canada formerly consisted of almost pure nickel. *Constantan*, an alloy of nickel and copper (2:3), is used in the construction of instruments where the electrical resistance must not change with temperature. *Manganin* and *nichrome* are alloys used as resistance wires in electrical apparatus. Nickel plating provides a coating that is resistant to corrosion and can be highly polished. It has been largely replaced by chromium plating, although articles to be plated with chromium are generally plated first with nickel.

19. Compounds of nickel. *Nickelous oxide*, NiO, may be prepared by heating nickelous hydroxide, $Ni(OH)_2$, which has been precipitated from nickelous salts in solution by addition of a soluble hydroxide. *Nickelous chloride* may be made by treating the oxide with hydrochloric acid and crystallizes from solution as the hexahydrate.

20. The platinum metals of Group VIII. We have seen that iron, cobalt and nickel formed a triad of elements which fitted in between two long periods of the periodic table. There are two other similar triads, also placed in Group VIII. These are *ruthenium*, *rhodium* and *palladium*; and *osmium*, *iridium* and *platinum*. There are some likenesses between these elements and iron, cobalt and nickel, but they are so much like platinum that they are known as the *platinum metals*. Because of its importance we shall discuss platinum in more detail than the others.

Platinum is a white metal with a melting point of 1755°C. and a specific gravity of 21.5. It is ductile and malleable, and somewhat harder than gold. It adsorbs gases readily when it is in a finely divided state and its value as a catalyst

may depend upon this property. It is used as a catalyst in many reactions, the most important being the Ostwald process for the production of nitric acid, the Haber process for the production of ammonia, and the contact process for the preparation of sulphuric acid. The metal is not attacked by oxygen even at high temperatures but it unites with chlorine. It does not dissolve in simple acids but it dissolves in aqua regia forming *chloroplatinic acid*, H_2PtCl_6.

Platinum is used in jewellery, in dentistry, in electrical instruments, as a catalyst, and in the manufacture of laboratory utensils. In the use of platinum utensils in the laboratory attention must be paid to the effect of fused alkalis, free chlorine, and metals which will alloy with platinum. The use of platinum depends upon its resistance to oxygen and to most reagents, and upon its high melting point. Platinum has the same coefficient of thermal expansion as soda glass and it is used in the laboratory where electrical conductors must be sealed into soft glass, although in industry there are alloys which can be used for this purpose.

While platinum has positive valences of 1, 2, 3, 4, or 6, the important compounds are those in which the valence is 2 or 4. It forms two chlorides, $PtCl_2$, and $PtCl_4$, which react with an excess of hydrochloric acid to form complex acids. $PtCl_2$ forms *chloroplatinous acid*, H_2PtCl_4, and $PtCl_4$ gives *chloroplatinic acid*, H_2PtCl_6.

Question Summary

1. Name the metals of the three triads in the long periods of the periodic table.

2. (*a*) Describe the early production of iron.
(*b*) Where does iron occur on the earth?

3. (*a*) Describe a blast furnace.
(*b*) What are the reactions which explain the operation of a blast furnace?
(*c*) Name two important by-products of a blast furnace and indicate their uses in industry.

4. (*a*) How is cast iron produced?
(*b*) What is the difference between white and grey cast iron and what effect does it have on their properties?
(*c*) How is malleable cast iron produced and what are its properties?

5. (*a*) Describe a reverberatory furnace.
(*b*) What are the properties and uses of wrought iron?

6. (*a*) What are the differences between steel and iron?
(*b*) Describe the Bessemer process for making steel.
(*c*) Describe the open hearth process for making steel.
(*d*) What is crucible steel?

7. (*a*) Indicate the changes which occur in steel with temperature.
(*b*) Explain the principles of the tempering of steel.
(*c*) What is case-hardened steel and how is it produced?

8. (*a*) Explain why other elements are added to steel to produce alloys.
(*b*) Give the approximate composition and properties of some alloy steels.

9. (*a*) What are the properties of pure iron and how may it be produced in the laboratory?
(*b*) What are the chemical properties of iron?

10. (*a*) Describe some ferrous compounds and their reactions.
(*b*) What is the principle of blue-black writing ink?

11. (*a*) What are the general properties of ferric compounds?
(*b*) Describe the production and use of Russia iron.
(*c*) Give some properties of ferric hydroxide and ferric chloride.

12. (*a*) How is Prussian blue prepared and what are its uses?
(*b*) How is Turnbull's blue prepared?

13. Describe the principle of the preparation of blueprints.

14. How does cobalt occur on the earth?

15. (*a*) What are the properties of cobalt?
(*b*) What are stellite and carboloy and what are their uses?

16. Describe the cobalt compounds.

17. (*a*) Where does nickel occur on the earth?
(*b*) How is it obtained from its ores?

18. (*a*) What are the properties of nickel?
(*b*) Name some important alloys of nickel.

19. Name some of the compounds of nickel.

20. (*a*) What are the platinum metals?
(*b*) What makes platinum useful in jewellery?
(*c*) What makes platinum useful in industry?
(*d*) What substances attack platinum?

Chapter **41**

Copper, Silver and Gold

1. Introduction. *Copper*, *silver*, and *gold* appear in Group I of the periodic table, together with the alkali metals, but they are different from them. They are not oxidized readily and are found at the bottom of the electrochemical series, while the alkali metals are oxidized easily and are at the top of the series. The alkali metals all have a positive valence of 1, while the most familiar compounds of copper show a valence of 2, and those of gold have a valence of 3. However, the silver compounds and some compounds of copper have a valence of 1. The oxides of the alkali metals are decidedly more basic than the oxides of copper, silver, or gold, and the latter metals show a pronounced tendency to form complex ions.

COPPER

2. Occurrence. Copper was known to prehistoric man, probably because it occurred in the free state and did not require any metallurgical treatment. Copper implements that are more than six thousand years old have been discovered. The name is derived from *aes cyprium* (Cyprian brass), the name given by the Romans to the metal obtained from the mines of Cyprus. The name was altered to *cuprum* from which the modern symbol "Cu" is derived.

Copper is found in the free state in many parts of the world. The most important deposits of free copper are south of Lake Superior in the United States, but some are found along the Coppermine River in Canada, in Sweden and in Russia. Some of the copper ores are *cuprite*, Cu_2O,

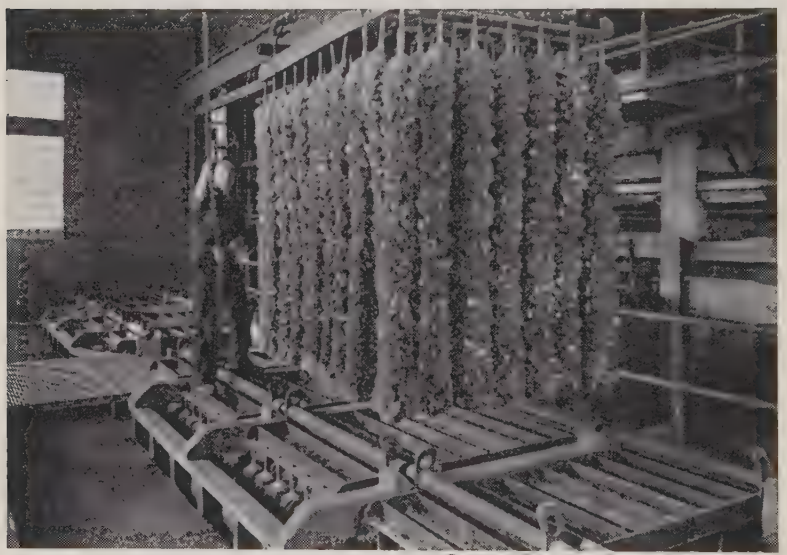
melaconite, CuO, *malachite*, $Cu(OH)_2.CuCO_3$, *chalcocite*, Cu_2S, and *chalcopyrite*, $CuFeS_2$.

3. Metallurgy. When the copper is in an ore not containing other metals, the ore is ground and heated with a flux, which forms a slag with the *gangue* or earthy portion of the ore. The slag floats on the top of the liquid copper. If the metal is in the form of cupric oxide, hydroxide, or carbonate, the ores may be leached with dilute sulphuric acid which dissolves the copper and forms a solution of cupric sulphate. The copper is recovered from the solution by electrolysis.

The most important ores are the sulphides which are ground and concentrated by *flotation* (see Chap, 39, sec. 3). The concentrated ore which is removed from the froth is roasted to remove some of the sulphur as sulphur dioxide. The ore is then treated in a blast furnace with silica or limestone, depending upon whether the ore contains an excess of iron or silica. Some of the iron is removed in the slag and the product, known as a *matte*, consists of a mixture of copper and iron sulphides. The matte is placed in a converter lined with magnesite brick. Again the iron is removed in the slag and the sulphur converted to sulphur dioxide. As the melted copper solidifies it gives off some dissolved sulphur dioxide and forms large blisters, which give the name of *blister copper* to the product. The blister copper contains some cuprous oxide and this is converted to copper by melting the metal with powdered coal, which acts as a reducing agent. Sometimes the carbon is introduced into the molten metal by stirring with wooden rods. The molten copper is cast into large plates which serve as anodes in electrolytic refining.

In the electrolytic process pure sheet copper acts as the cathode, and the impure copper plates as the anode. The electrolyte is dilute sulphuric acid and copper sulphate. The impure copper goes into solution at the anode and pure copper is plated out at the cathode. The impure copper contains

zinc, silver and gold, together with small quantities of palladium and platinum. The zinc being above copper in the activity series does not plate out with the copper but remains in solution. The noble metals fall to the bottom of the cell as *anode mud*. This mud is an important source of silver and gold, and the recovery of these metals often pays the cost of the refining of the copper.



Courtesy Canadian Copper Refineries Ltd.

Fig. 219. A mass of copper sulphate crystals produced during electrolysis.

4. Properties and uses. Copper is useful mainly because of its excellent conduction of heat and electricity. Its other physical properties are: reddish colour in reflected light, flexibility, malleability, ductility, low specific heat and its moderate density of 8.94 grams per cubic centimetre. Its greatest disadvantage as a metal is its lack of hardness.

Because of its excellent electrical conductivity large quantities of it are used in electrical apparatus and wiring. For this purpose it must be very pure as small amounts of impurities increase the resistance.

Its excellent heat conductivity makes it very desirable for tubes and vessels through which heat must be transferred to solutions. It was once widely used for cooking utensils but is now only used on the outside of the bottom. It oxidizes rapidly at moderate temperatures so it is not suitable for high-temperature work.

Copper is just below hydrogen in the electrochemical series so it is not attacked by non-oxidizing acids. For example, it does not dissolve in dilute hydrochloric or sulphuric acid unless oxygen is present to convert it to the oxide. If concentrated sulphuric acid or nitric acid is used it dissolves readily, reducing the acid at the same time.

$$Cu + 2\ H_2SO_4 \longrightarrow CuSO_4 + 2\ H_2O + SO_2$$
$$Cu + 4\ HNO_3 \longrightarrow Cu(NO_3)_2 + 2\ H_2O + NO_2$$

It also dissolves in dilute nitric acid.

$$3\ Cu + 8\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO$$

The lack of chemical activity makes copper very desirable wherever corrosion resistance is desired. It is widely used for high-quality plumbing systems, roofing, water tanks, flashings under windows and facings and for covering the hulls of wooden ships. In moist air it becomes coated with a basic carbonate or sulphate which is green in colour and gives the roof a less metallic tone. It does not corrode readily in salt water and it has a poisonous effect on marine organisms so it is used on ship's hulls and in marine paints.

Copper combines directly with several non-metals at higher temperatures. The union with oxygen in the flame is intriguing because of the colour of the two oxides. Cuprous oxide, Cu_2O, is a ruby red colour and appears in the semi-reducing portion of the flame. Cupric oxide, CuO, appears as a black coating where oxygen is abundant.

Although it is not very hard it will wear many times as long as type metal which is largely made of lead. It is readily

deposited by electrolysis on a wax base coated with graphite to make it a good conductor. The type is used to make an impression in the wax and copper is then deposited in the impression. When the wax is melted away an exact one-piece copper duplicate of the original type is obtained. It is backed with lead and is then an *electrotype* ready to print hundreds of thousands of copies of a page like this.

Copper is used to make many important alloys. *Brass* is an alloy of copper and zinc, and *bronze* an alloy of copper and tin, but the terms brass and bronze are applied to a large number of alloys of copper with varying amounts of other metals. *Gun metal* contains copper, zinc, tin and lead. *German silver* contains copper, nickel and zinc. *Britannia metal* contains copper, tin, lead and antimony. Copper is used in coinage, such as the familiar one-cent piece, and silver and gold coins contain about 10 per cent of copper.

5. Oxides of copper. *Cuprous oxide*, Cu_2O, is found in nature as the mineral known as *ruby copper*. It may be prepared in the laboratory by gently heating copper in the air, or by reducing cupric compounds in the presence of an alkali.

Cupric oxide, CuO, is a black powder produced by heating copper in air or oxygen, or by heating the hydroxide, carbonate, or nitrate of copper. It is insoluble in water but dissolves in dilute acids to produce cupric salts. It is a good oxidizing agent because of the ease with which it can be reduced (see Chap. 6, sec. 7).

6. Cuprous compounds. *Cuprous chloride*, CuCl, is a white insoluble salt, which resembles silver chloride, and can be prepared by heating a cupric chloride solution in the presence of hydrochloric acid and copper turnings.

$$CuCl_2 + Cu \longrightarrow 2\ CuCl$$

Cuprous sulphide, Cu_2S, may be prepared from cupric sulphide by heating it in the absence of air or reducing it by means of hydrogen.

$$2\ CuS \longrightarrow Cu_2S + S$$
$$2\ CuS + H_2 \longrightarrow H_2S + Cu_2S$$

It is very easily made by heating copper turnings or wire in a covered vessel with an excess of sulphur to displace the air.

$$2\ Cu + S \longrightarrow Cu_2S$$

7. Cupric compounds. *Cupric hydroxide*, $Cu(OH)_2$, appears as a blue gelatinous precipitate when a soluble hydroxide is added to a solution of a cupric salt. *Bordeaux mixture* contains lime and cupric hydroxide as a precipitate and is used as a spray for plants to prevent the growth of fungi (see Chap. 36, sec. 20).

Cupric chloride, $CuCl_2$, may be made by treating the oxide, hydroxide, or carbonate with hydrochloric acid, and it crystallizes from solution as the blue hydrate, $CuCl_2.2H_2O$, although the anhydrous salt is yellow. The addition of ammonium hydroxide to a solution of cupric chloride forms first the basic chloride which precipitates and then dissolves in an excess of hydroxide to form the deep-blue *copper-ammonium chloride*, $Cu(NH_3)_4Cl_2.H_2O$.

$$CuCl_2 + 4\ NH_4OH \longrightarrow Cu(NH_3)_4Cl_2.H_2O + 3\ H_2O$$

Cupric bromide, $CuBr_2$, is obtained as jet-black crystals from the evaporation of bromine water which has been treated with copper. When anhydrous cupric bromide is heated, bromine is given off and cuprous bromide remains.

Cupric sulphate, $CuSO_4$, is the most important commercial salt of copper. It can be made by treating the oxide or carbonate with sulphuric acid. It crystallizes from solution in the form of the familiar blue crystals of the pentahydrate, $CuSO_4.5H_2O$ which is known as *blue vitriol* or *bluestone*. There are other hydrates of cupric sulphate, and any of them will give the white anhydrous salt when heated. Anhydrous cupric sulphate turns blue in the presence of water, because of the formation of the cupric ion, and may be used as a test for water. Cupric sulphate is used in the manufacture of other copper compounds: Fehling's solution, insecticides,

germicides, fungicides, and paint pigments. It is sometimes used in small quantities in water reservoirs to destroy algae. It is used as an electrolyte in copper plating.

SILVER

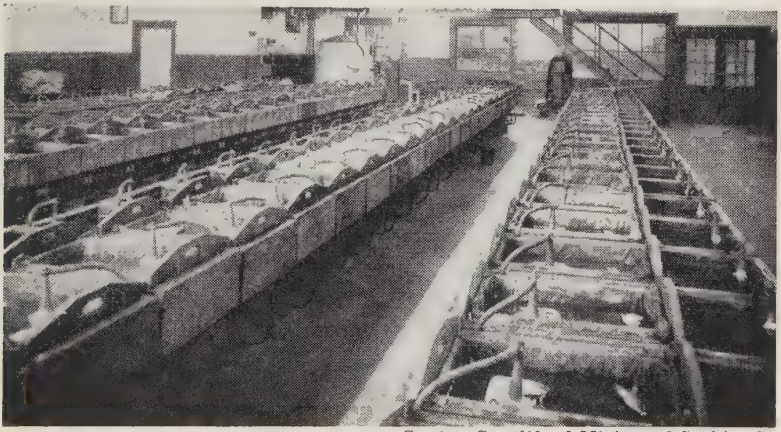
8. Occurrence. Silver has been known since ancient times. It has been valued by man because of its bright lustre and its resistance to corrosion. It has been used in coinage for many years.

Silver is found in the free state, usually alloyed with copper, gold, or mercury. It is sometimes found in large masses, but generally as small flakes scattered throughout rock. The principal ore is the sulphide, *argentite*, or *silver glance*, Ag_2S, which is found alone or mixed with *lead sulphide* or *galena*, PbS. Considerable amounts of silver are obtained during the refining of copper, nickel, and lead, since silver sulphide is often mixed with the sulphides of these metals. The chief supplies of silver come from Mexico, Ontario, and the Rocky Mountains.

9. Metallurgy. Ores containing metallic silver may be treated with mercury to form an amalgam which is separated from the rest of the ore and distilled in a retort. The mercury distils over and the silver remains in the retort. The mercury can be used again in the process. The same types of ore, together with those containing silver chloride, are pulverized and treated with a solution of sodium cyanide. Complex cyanides, as $NaAg(CN)_2$, are produced, and the silver may be recovered from the cyanide solution by adding powdered aluminum or zinc which will displace the silver.

Parke's process, by which silver is separated from lead, depends on the fact that molten zinc and lead are practically insoluble in one another, and silver is more soluble in zinc than in lead. The lead containing silver is melted and some zinc is added and well mixed. After a time the zinc rises to the top, carrying with it almost all of the silver, and may be skimmed off. The zinc-silver alloy is then heated in a furnace, and the zinc distilled

off to be used again in the process. The silver is refined electrolytically. Impure silver plates (Doré metal) form the anode, pure silver the cathode, and silver nitrate serves as the electrolyte. Pure silver is deposited on the cathode and any gold which may be present is caught as a powder in a bag suspended around the anode.



Courtesy Consolidated Mining and Smelting Co.

Fig. 220. Refined silver and gold are produced from Doré metal in Thum electrolytic cells. The diaphragm catches the gold.

10. Properties and uses of silver. Silver is intermediate between copper and gold in hardness. It is the best conductor of electricity and heat, and it is one of the most malleable and ductile of all the metals.

Silver is one of the least active metals. It does not combine directly with oxygen and it does not dissolve in dilute acids. It dissolves in strong oxidizing acids, such as nitric and sulphuric acids, to form silver salts. It has a great tendency to unite with sulphur, and the black tarnish which forms on silver is due to the formation of silver sulphide. Silver will tarnish quickly if left in contact with any articles containing sulphur, such as eggs and vulcanized rubber. This tarnish may be observed on spoons used for eating eggs, and may be demonstrated by leaving a silver coin for a few days with a rubber band wrapped around it.

Silver forms alloys with many metals, and as some of these alloys are harder than pure silver, they are often used for coinage, tableware and ornaments. The metal is used to prepare silver nitrate, silver halides and other silver compounds. When a solution of silver nitrate containing a small amount of ammonium hydroxide is treated with certain organic compounds, such as formaldehyde or glucose, the silver salt is reduced to the metal which is deposited as a bright film on the clean surface of the vessel containing the solution. Silver mirrors are made by a similar process.

11. The oxide of silver. *Silver oxide*, Ag_2O, may be obtained as a pale brown precipitate by the addition of a soluble hydroxide to a solution of a silver salt. It is not very stable, and decomposes rapidly into silver and oxygen when heated moderately. It dissolves in ammonium hydroxide to form a soluble silver-ammonium compound like those formed by copper and ammonium hydroxide.

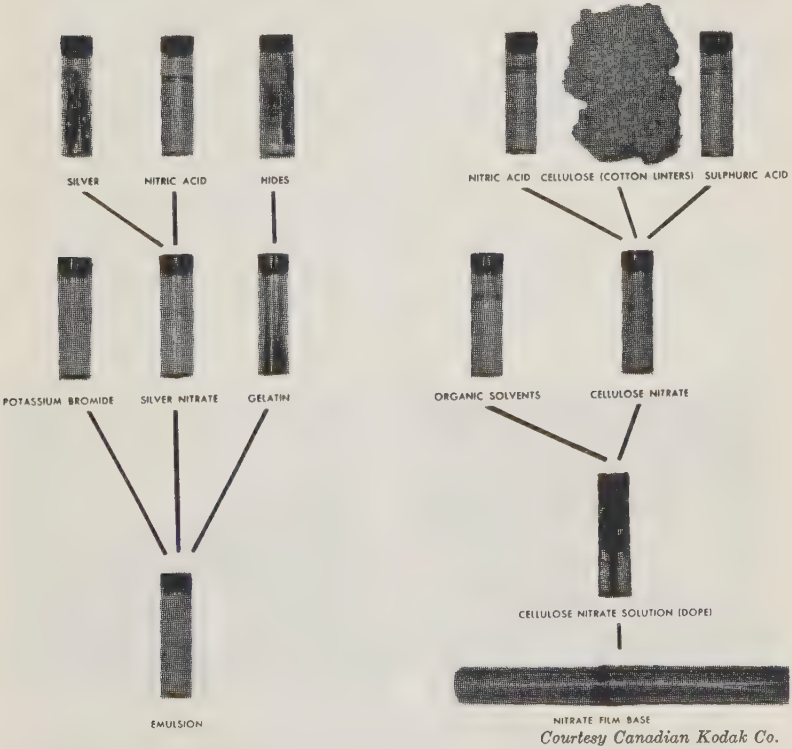
12. The silver halides. *Silver chloride*, AgCl, *silver bromide*, AgBr, and *silver iodide*, AgI, are formed as curdy precipitates when the solution of a silver salt is added to the solution of the halide. The chloride is white, the bromide is pale yellow, and the iodide is yellow. When exposed to light the silver halides become first violet and then brown in colour, due to the formation of metallic silver which becomes dispersed in the solid. The halogen is set free. This behaviour of the silver halides is the basis of photography.

You will recall that the chlorides of silver, lead and mercurous mercury are precipitated as a group when a chloride is added to a mixture of these ions. The lead chloride may be removed by washing with hot water and the silver chloride dissolves in ammonia.

$$AgCl + 2\ NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2\ H_2O$$

The $Ag(NH_3)_2^+$ is known as the silver ammonia complex ion. It is formed when any silver compound dissolves in ammonia.

13. Photography. A photographic plate or film consists of a glass plate or transparent film coated with an emulsion which consists of colloidal particles of silver halides suspended in gelatin. In some emulsions other substances, such as certain dyes, are also present. When exposed to light in a camera, the image is projected upon the surface of the film where the silver halides are rendered more sensitive to reduction to metallic silver in proportion to the amount of light which falls upon them. The portions of the image which are the brightest will therefore cause the greatest change in the emulsion. To develop the exposed film it is treated with a photographic developer, which consists of an alkaline reducing



Courtesy Canadian Kodak Co.

Fig. 221. The chemicals used in the making of photographic film.

agent, such as pyrogallol or hydroquinone, in the presence of sodium carbonate. The developer reduces the silver halide to metallic silver. Those portions which have received the most light will be reduced to the greatest extent. The portions of the film which have not been exposed to the light will not be affected by the developer. Since the unexposed parts of the film are still sensitive to light the developing process must be carried out in the dark or in a dim red light, depending upon the sensitivity of the film. Before being exposed to light, the developed film must be treated with a "fixing" solution of sodium thiosulphate which dissolves any silver halide left on the film. The film is now washed and dried, and has become a *negative*. The dark portions of the picture are represented by the lighter portions of the negative, since the silver halide in those parts of the film was not acted upon by the light, and has now been removed by the fixing solution. The brightest portions of the picture will be represented by the dark portions of the negative where there is the greatest reduction to metallic silver. Very finely divided metals usually appear black. The intermediate portions of the picture will be represented on the negative by varying densities of silver.

Fig. 222. Left, a negative showing how the light darkens the film with free silver, and right, a positive print made by shining light through the negative.

The printing of the picture is exactly the same process, but the emulsion is on a piece of paper which is placed next to the negative and exposed to light. The exposed paper is now developed and fixed in a similar way as was the film, but the picture is now a true representation of the original, since the portions of light and dark in the negative have been reversed. The emulsion used on the paper is different from that used on the film and is not so rapid in its action. It may be modified so as to supply various degrees of contrast between the light and dark portions of the picture.

14. Other compounds of silver. *Silver nitrate*, $AgNO_3$, is one of the most important compounds of silver. It may be prepared by dissolving silver in concentrated nitric acid. It is used in medicine under the name of *lunar caustic* to cauterize wounds, since it has a strong oxidizing action. When the salt is placed upon the skin, black metallic silver is deposited by the action of reducing agents in the skin. The same action takes place when it is placed on cloth, and it is used as an ingredient in indelible marking inks.

Silver carbonate, Ag_2CO_3, is slightly yellow in colour and may be precipitated from solutions of silver salts by any soluble carbonate. *Silver sulphate*, Ag_2SO_4, may be made by the action of concentrated sulphuric acid upon silver. *Silver sulphide*, Ag_2S, is precipitated by hydrogen sulphide from solutions of all silver compounds, whether free acid is present or not.

GOLD

15. Occurrence. Since it occurs in the free state, and can be obtained without a knowledge of metallurgical processes, gold was well known to primitive man. Its rarity, durability, appearance, and ease of working made it highly prized for ornaments. Man has used it as a medium of trade and a standard of value for many years.

Gold is almost always found in the free state, either as nuggets or as small flakes in veins of quartz or in alluvial sands. Native gold usually contains some silver or platinum. It occurs in small quantities in the sulphide ores of metals like lead and copper, and it is present in sea-water. The chief gold-producing countries are Africa, the United States, Russia and Canada, but it is found in many other countries.

National Film Board photo

Fig. 223. Panning for gold in the Yukon only a mile from the Alaska Highway.

16. Metallurgy. In early days gold in alluvial sands was obtained by *panning*. The sandy material was placed in shallow pans and washed with water. The heavier particles of gold sank to the bottom and the sand was washed over the edge of the pan. *Placer mining* is the same as panning but on a larger scale. The deposits are placed in long troughs and the sand is carried away by streams of water. In

hydraulic mining, powerful streams of water are directed against the sand which is washed into sluices where the gold will settle and the lighter material will be washed away.

Gold which is present in quartz rock must be recovered by amalgamation with mercury, the cyanide process, or the chlorine process. In all cases the quartz ores are first pulverized. In the amalgam process, the gold in the crushed rock is amalgamated with mercury by rolling them in a barrel. The gold dissolves in the mercury to form an amalgam which is placed in a retort and the mercury distilled off. In placer mining mercury is sometimes placed between cleats in the bottom of the trough and an amalgam thus formed.

In the cyanide process, the crushed ore or material which has already been worked in placer mining, is treated with a solution of sodium or potassium cyanide in the presence of air. The gold is converted into a complex cyanide.

$$4\ Au + 8\ NaCN + O_2 + 2\ H_2O \longrightarrow 4\ NaOH + 4\ NaAu(CN)_2$$

The gold is recovered from solution by electrolysis or by the addition of zinc. This process is slow and the ore must remain in contact with the cyanide for several days before the reaction is completed.

In the chlorine process the crushed ore is treated with chlorine. The chlorine unites with the gold to form *auric chloride*, $AuCl_3$, from which the gold may be obtained by electrolysis.

17. Properties of gold. Gold is the most malleable and ductile of all the metals. It is too soft for most purposes when it is pure and it is usually alloyed with copper. The purity or fineness of gold is represented by *carats*, which indicate the number of parts of gold in 24 parts of the alloy. Eighteen-carat gold means that 18/24 of the metal is pure gold. Alloys which are more than 18 carat pure are too soft for most

purposes, but gold coins are about 21 carats, which is about 90 per cent gold.

Gold does not combine with oxygen, nor does it react with hydrogen sulphide or the common acids. It dissolves in *aqua regia*, which is a mixture of hydrochloric and nitric acids. This mixture supplies chloride ion and chlorine which produces *chlorauric acid*, $HAuCl_4$ (see Chap. 19, sec. 9). For the same reason, chlorine water dissolves gold.

Question Summary

1. What is the chief difference between the metals copper, silver and gold, and the alkali metals?

2. Where does copper occur on the earth?

3. (*a*) How is copper obtained from its ores?
(*b*) Define blister copper, anode mud.

4. (*a*) What are the chief physical and chemical properties of copper?
(*b*) What are the chief uses of copper and how do they depend on these properties?
(*c*) Name some alloys containing copper.

5. Discuss the oxides of copper.

6. Describe the cuprous compounds.

7. (*a*) Describe the cupric compounds.
(*b*) What is Bordeaux mixture?
(*c*) Describe the reaction between cupric salts and ammonia.
(*d*) What are the chief uses of cupric sulphate?

8. In what forms is silver found on the earth?

9. (*a*) How is silver obtained from its ores?
(*b*) Describe Parke's process.

10. (*a*) What are the properties of silver?
(*b*) What are the uses of silver which depend on these properties?

11. Describe the oxide of silver.

12. Describe the halides of silver.

13. Describe the chemical action of photography.

14. Describe some of the compounds of silver.

15. How does gold occur in nature?

16. How is gold obtained from its ores?

17. What are the properties of gold?

Chapter **42**

Zinc, Mercury and Other Metals

1. Introduction. We have discussed the important transition elements of Group VIII and Group I-B in some detail in the two previous chapters and we wish to mention the remaining ones in this chapter.

In Group II-B, zinc, cadmium and mercury have an inner shell of eighteen electrons. In this respect they are not true transition elements because they have complete inner shells of electrons but they complete the transition process so we class them with the others. They will show little tendency toward variable valence and will have colourless ions. Zinc and mercury are very important elements and cadmium is widely used for electroplating.

In Group III-B we have scandium, yttrium and the fifteen rare earth elements which all have one or more incomplete shells of electrons, variable valences and coloured ions. Actinium, a radioactive element, also occurs in this sub-group.

In Group IV-B we find titanium, zirconium, hafnium and thorium as other transition elements. Titanium promises to become an important industrial element but the others are little known. Thorium is very slowly radioactive. It really belongs to the actinide series.

In Group V-B we find vanadium, columbium, tantalum and protactinium. Vanadium is important as an alloying element for steel. Protoactinium is radioactive and like thorium should be in Group III-B.

In Group VI-B, chromium, molybdenum, tungsten and uranium are all relatively important elements: the first two

as alloying elements for steel; tungsten for very high temperature work as in the filaments of electric lights and spark-gap tips; and uranium as the material for atomic bombs and nuclear energy sources.

In Group VII-B manganese is the important element, while masurium and rhenium are almost unknown. The atomic weight of masurium has not been checked because of the lack of enough material.

All these elements are characteristic transition elements and a great deal of chemistry is involved in their properties and those of their compounds. We will only discuss the more common elements, starting with Group II-B. Zinc and cadmium are quite alike in their properties but mercury resembles silver and gold more than it does zinc and cadmium.

ZINC

2. Occurrence. An alloy called *brass*, made from zinc and copper, was known to the ancients, and articles made of zinc which date to a time before the Christian era have been discovered. The most important ores, with their North American names, are *zincite*, ZnO; *sphalerite*, ZnS; *smithsonite*, $ZnCO_3$; and *calamine*, $Zn_2H_2SiO_5$. Sphalerite, which is also called zinc blende, is the predominant form in the Canadian fields near Trail, B.C., Flin Flon, Manitoba, in the Yukon Territory and near Quebec City.

3. Metallurgy. The treatment of zinc ores is no different from the usual steps in metallurgy. The sulphide ores are crushed, concentrated by flotation, and roasted to remove the sulphur. The carbonate ores are roasted to form the oxide, which is then reduced by heating with powdered coal. Because zinc is a volatile metal the reduction is carried out in retorts from which the metal is obtained as a vapour. Fireclay receivers are fastened to the retorts to collect the con-

densed vapour. The carbon monoxide which is produced burns at the mouth of the retort.

Electrolytic methods are now in general use. For example, at Flin Flon, Manitoba, the ores are crushed and roasted and are then leached with dilute sulphuric acid. The resulting solution of zinc sulphate is treated with metallic zinc to precipitate the less active metals, such as copper, lead, silver and cadmium, and is then electrolyzed. The metal obtained by the electrolytic process is very pure.

Courtesy Consolidated Mining and Smelting Co.

Fig. 224. Zinc is plated out on aluminum cathodes from zinc sulphate solutions.

4. Properties and uses. Zinc is a silvery metal which is hard and brittle at ordinary temperatures. Between 100°C. and 150°C. it becomes malleable and can be rolled and drawn into wire. Above 200°C. it is no longer malleable and becomes brittle again. These changes are due to the existence of allotropic forms of the metal. Zinc melts at 419°C., boils at 907°C., and has a specific gravity of 7.1.

Zinc burns in air with a bluish flame, giving the oxide, ZnO. The metal does not corrode in air, since it becomes covered with a protective coating of the basic carbonate, $Zn_2(OH)_2CO_3$.

Zinc does not displace hydrogen from boiling water, but it does displace it from steam. Pure zinc reacts slowly with hydrochloric and sulphuric acids, because the hydrogen which is liberated forms a protective film on the surface. Ordinary commercial zinc, which contains many impurities, reacts rapidly with acids. The metal reacts with nitric acid to form oxides of nitrogen, or ammonium nitrate, depending on the temperature and the concentration of the acid.

Zinc dissolves in solutions of strong bases, giving off hydrogen and forming *zincates*. With sodium hydroxide we have

$$\mathbf{Zn + NaOH + H_2O \longrightarrow NaHZnO_2 + H_2}$$

In the presence of an excess of the hydroxide the normal zincate Na_2ZnO_2 will be formed instead of the acid salt as shown above.

One of the most familiar uses of zinc is in the manufacture of *galvanized iron*, in which the surface of the iron is protected by a coating of zinc. This coating may be obtained by dipping clean iron sheets into molten zinc, by spraying the sheets with molten zinc, or by electroplating. Since the film of basic carbonate which forms on the zinc surface is adherent, it protects the metal from further action. *Sherardized iron* is made by covering the iron with zinc dust and zinc oxide and baking it.

Zinc is used in alloys such as aluminum solder and German silver, and large quantities of the pure metal are used in the manufacture of dry cells. It is used in Parke's process for separating silver from lead (see Chap. 41, sec. 9), for making gutters and cornices on buildings, and in the laboratory as a reducing agent.

5. The oxide and hydroxide of zinc. *Zinc oxide*, ZnO, is a white powder which may be obtained by burning zinc or by roasting the sulphide ores. It is white when cold and

yellow when heated. It is used in paints as the pigment known as *zinc white*. Since zinc sulphide is white, paints containing zinc oxide will not darken when exposed to hydrogen sulphide, and are useful for interior painting. The most important use of zinc oxide is in the manufacture of automobile tires, where it is used as a filler. It is also used in medicine, in dentistry, and in the preparation of glass and enamels.

Zinc hydroxide, $Zn(OH)_2$, appears as a white precipitate when alkalis are added to solutions of zinc salts. It is an amphoteric substance as it reacts with both acids and bases. With acids it gives zinc salts.

$$\mathbf{Zn(OH)_2 + 2\ HCl \longrightarrow ZnCl_2 + 2\ H_2O}$$

With bases it acts as an acid, H_2ZnO_2, to give zincates.

$$\mathbf{H_2ZnO_2 + 2\ NaOH \longrightarrow Na_2ZnO_2 + 2\ H_2O}$$

It dissolves in ammonium hydroxide to produce a colourless complex zinc-ammonia ion which is similar to the behaviour of copper.

6. Other compounds of zinc. *Zinc chloride*, $ZnCl_2$, is a white deliquescent solid obtained by the action of hydrochloric acid upon the metal or the oxide. It is the fungicide used to impregnate wood to prevent decay and is employed in making parchment paper. Since zinc chloride dissolves metallic oxides, it is used to prepare metallic surfaces for soldering and is the chief constituent of acid soldering fluxes.

Zinc sulphate, $ZnSO_4$, may be obtained by treating the metal or the oxide with sulphuric acid, or by roasting the sulphide ores and leaching with water. It crystallizes from water as the heptahydrate, $ZnSO_4.7H_2O$. It is used as a preservative for hides, as a mordant in dyeing, in medicine, and in the manufacture of lithopone (see Chap. 33, sec. 18).

CADMIUM

7. Occurrence and metallurgy. Cadmium was discovered in 1817 by Stronmeyer in the flue dust of a zinc furnace. It is more easily reduced than zinc, and it is more volatile, so that it is present in the first portions of zinc which condense from the retorts.

8. Properties and uses. Cadmium is a silvery-white metal with a bluish tinge. It is softer than zinc and more malleable, although it becomes more brittle when heated. Cadmium is used on skates and hardware as an electroplate because it protects steel like zinc does.

9. Compounds of cadmium. *Cadmium oxide*, CdO, is a brown substance formed by burning the metal in the air. *Cadmium hydroxide*, $Cd(OH)_2$ is precipitated as a white substance from solutions of cadmium salts. It is more basic than zinc hydroxide and it is not amphoteric.

Cadmium sulphide, CdS, is a yellow substance thrown down by hydrogen sulphide from moderately acid solutions of cadmium salts. It is used as a pigment in paints.

MERCURY

10. Occurrence and metallurgy. Mercury was mentioned by Theophrastus in 300 B.C. as "liquid silver" and the modern symbol Hg comes from the Latin "hydrargyrum", which has that meaning. The element had a great fascination for the alchemists, who likened it to the swift messenger of the gods, and gave it its modern name, mercury. In many European countries it is called "quicksilver".

Mercury occurs in the free state in small quantities but the most important ore is the sulphide, *cinnabar*, HgS, which is found in Italy, Spain, Mexico and in the United States.

The metal is obtained quite easily from its ores, which are of low quality. They are concentrated by flotation, and roasted, when the mercury will be set free as a vapour.

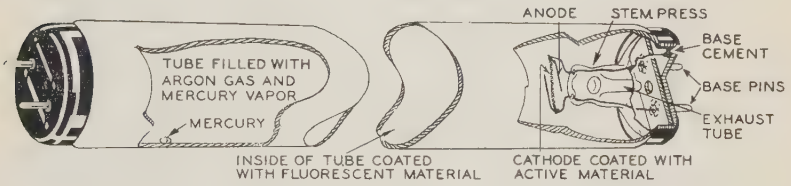
$$\mathbf{HgS + O_2 \longrightarrow Hg + SO_2}$$

The metal is purified by filtering it through chamois leather, washing it by allowing it to drop in a thin stream through nitric acid, and then redistilling.

11. Properties and uses. Mercury is a silvery liquid at ordinary temperatures. It freezes at $-39°C.$, boils at 357°C.

and has a specific gravity of 13.6. It is an excellent conductor of electricity, and is used frequently as a conducting liquid in electrical apparatus.

Because of its high specific gravity and low vapour tension, mercury is used in barometers and manometers. Since it has a uniform expansion rate, can be purified easily, and has convenient freezing and boiling points, it is used in thermometers. It forms an alloy, known as an *amalgam*, with many of the metals.



Courtesy Canadian General Electric Co.

Fig. 225. Ultra violet light from a mercury arc is changed to visible light by the coating on the fluorescent tube.

Mercury vapour does not conduct electricity when it is cold, but, when heated, an arc is produced in a tube containing the vapour. The light produced by this arc is rich in ultra-violet rays. If the tube is made of quartz, which transmits the ultra-violet light, it may be used in medical work and as an illuminant in photography. Modern fluorescent lights are mercury arcs with a phosphor coating on the tube which gives white light when irradiated with ultra-violet light.

Mercury unites with oxygen at a high temperature to form the red oxide. It also combines readily with sulphur and the halogens. Mercury has positive valences of 1 and 2, and thus forms two series of stable compounds. The compounds of higher valence are reduced easily to those of the lower valence, and with an excess of the reducing agent, to metallic mercury. For example:

$$2\,HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

12. Mercuric oxide, HgO, may be obtained as a red powder by heating mercury in the air, or by heating the nitrate. If a base such as sodium hydroxide is added to the solution of a mercuric salt, mercuric oxide will be precipitated as a yellow powder. The difference between the red and yellow forms of the oxide is due to the finer subdivision of the yellow form, otherwise they are identical. The yellow form changes to the red form when heated and is used to make heat-indicating paints.

13. Mercurous compounds. These are unusual in that mercury only appears to be monovalent. Two mercury atoms share a pair of electrons to form Hg_2, which then behaves as a divalent ion.

Mercurous chloride, Hg_2Cl_2, is the most important mercurous salt. It may be prepared by heating mercuric chloride with metallic mercury, or, since it is not very soluble, by adding a soluble chloride to a solution of mercurous nitrate. It is used in medicine under the name of *calomel*. Mercurous salts are very poisonous, but calomel may be used safely since it is so slightly soluble. Great care must be taken to see that there is no chance of confusion between calomel and the soluble poisonous mercuric chloride known as *corrosive sublimate*.

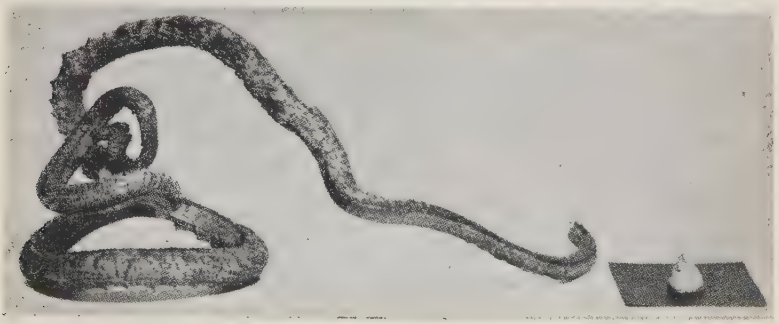
14. Mercuric compounds. *Mercuric chloride*, $HgCl_2$, sometimes called *bichloride of mercury* or *corrosive sublimate*, may be made by the direct union of mercury and chlorine, or by heating a mixture of mercuric sulphate and sodium chloride.

$$\mathbf{HgSO_4 + 2\ NaCl \longrightarrow Na_2SO_4 + HgCl_2}$$

This salt is very poisonous and great care must be taken in using it as an antiseptic. To prevent it being mistaken for other substances in the medicine chest, it is often sold in the form of blue tablets. White of eggs is used as an antidote because the mercuric chloride forms an insoluble substance with the albumin of the egg.

Mercuric fulminate, $Hg(ONC)_2$, is produced as a white precipitate when mercury is treated with nitric acid in the presence of alcohol. It decomposes on striking and is used in the manufacture of percussion caps to fire the powder in shells.

Mercuric thiocyanate, $Hg(CNS)_2$, is an interesting substance which may be precipitated by the addition of potassium thiocyanate to a solution of mercuric nitrate. When formed into small pellets and burned, it forms a voluminous ash known as "Pharaoh's Serpents".



Courtesy The Blakiston Company

Fig. 226. Mercuric thiocyanate gives a voluminous ash (Pharaoh's Serpents).

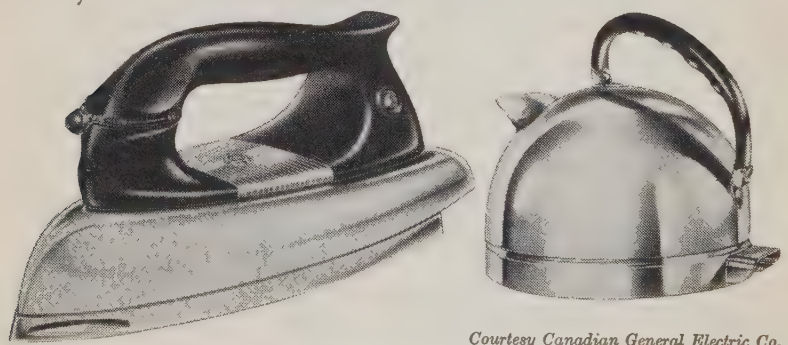
15. The Rare Earth Family. Scandium, yttrium, and the fifteen elements whose atomic numbers lie between 57 and 71 are known as the Rare Earth Family. The names of the rare earths and their symbols are given in the table of atomic weights. The rare earths resemble each other so strongly that for some time their existence as individual elements was not recognized. You will recall that structurally the rare earths differ from one another only in that the fourth shell of electrons is filling out from 18 to 32 electrons while the two outer shells have about the same number of electrons in each element. Since the outer shells determine the valence and properties these elements are extremely alike.

16. The metals of Group VI-B. Group VI of the periodic table consists of the non-metals, oxygen, sulphur, selenium and tellurium; and the metals, *chromium*, *molybdenum*, *tungsten* and *uranium*. Unlike the metals of Group V-B the metals of Group VI-B are of considerable importance, and form several compounds that have many uses. We will therefore mention them in many separate sections.

17. Occurrence and metallurgy of chromium. Chromium was discovered by Vauquelin in 1798. It occurs in small amounts with aluminum in some rocks. It makes the ruby (Al_2O_3) red and the emerald (beryllium aluminum silicate) green. Its principal ore is *chromite*, $Fe(CrO_2)_2$. About half of the world's supply of chromite comes from Rhodesia, and there are deposits in the United States.

Pure chromium may be obtained by the Goldschmidt process by treating the oxide with aluminum powder. The metal may also be obtained as an electroplate by the electrolysis of chromic acid to which sulphates, borates, or phosphates are added.

18. Properties and uses of chromium. Chromium is a very hard silvery metal which does not tarnish in the air so is widely used as a decorative and protective coating on steel and other metals. Its chief use is in making stainless steel where it inhibits the rusting of iron and converts the whole alloy to a passive state where it is not attacked by acids. It is widely used in the chemical industries.



Courtesy Canadian General Electric Co.

Fig. 227. A chromium plate resists corrosion and maintains a high polish.

19. Uranium was discovered in 1789 by Klaproth in the mineral *pitchblende* which contains the oxide, U_3O_8, together with the oxides of other elements. Pitchblende is found in the Belgian Congo, in Canada and in Austria. The chief interest in uranium minerals has been in their radium content, but

they have now a greater interest since the discovery of the use of uranium in atomic fission. The metal may be obtained by the reduction of the oxide in an electric furnace.

Uranium is a white metal which combines slowly with oxygen in the air and forms salts with the common acids. Its common valences are 4 and 6. Other valences are known but the compounds are not stable in aqueous solution.

20. Manganese. Group VII of the periodic table consists of the non-metallic halogens, the metals *manganese*, *masurium* and *rhenium*, and the newly-discovered element with atomic number 85. Of these elements the only one of importance is manganese, isolated by Gahn in 1774 following the experiments of Scheele on the preparation of chlorine from manganese dioxide. Its most important ore is *pyrolusite*, MnO_2. It also occurs in other oxides such as *braunite*, Mn_2O_3, *manganite*, MnO(OH) and *hausmanite*, Mn_3O_4.

Pure manganese is difficult to prepare and has no commercial value. Alloys of iron and manganese are usually prepared by the simultaneous reduction of both metals in a blast furnace, and are used in the manufacture of steels for resisting abrasion and shock. *Spiegeleisen* contains about 10 per cent of manganese and *ferromanganese* about 75 per cent.

Manganese is a reddish-grey metal somewhat softer than iron, which it resembles in several of its properties. Pure manganese is oxidized in the air, but it is more resistant if carbon is present in the metal. It reacts slowly with water to displace hydrogen, and it dissolves in acids to form salts. Manganese forms five oxides and there are five corresponding series of salts.

21. Potassium permanganate, $KMnO_4$, is an oxidizing agent and its reaction depends upon whether it is used in acid or alkaline solution. If an alkali is added, a solution of potassium permanganate becomes green from the production of the manganate.

$$4\ KMnO_4 + 4\ KOH \longrightarrow 4\ K_2MnO_4 + 2\ H_2O + O_2$$

If any oxidizable material is present, the oxidation proceeds further and manganese dioxide is produced.

$$4\,KMnO_4 + 3\,C_2H_5OH \longrightarrow 4\,MnO_2 + KOH + 3\,KC_2H_3O_2 + 4\,H_2O$$

In acid solution, potassium permanganate gives a manganous salt.

$$10\,FeSO_4 + 8\,H_2SO_4 + 2\,KMnO_4 \longrightarrow 5\,Fe_2(SO_4)_3 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2O$$

$$5\,H_2SO_3 + 2\,KMnO_4 \longrightarrow 2\,H_2SO_4 + K_2SO_4 + 2\,MnSO_4 + 3\,H_2O$$

This reaction is used to determine iron or sulphur dioxide in quantitative analysis. The standardized permanganate solution is added until it is no longer decolorized. Potassium permanganate is a powerful oxidizing agent used in dyeing, as a bleaching agent, and in medicine.

Question Summary

1. (*a*) What are the important transition elements in Groups II to VII of the periodic table?
(*b*) How do the elements of the zinc sub-group differ from the others?

2. How does zinc occur on the earth?

3. How is zinc obtained from its ores?

4. (*a*) What are the properties of zinc?
(*b*) How are the uses of zinc related to its properties?

5. (*a*) What are the properties and uses of zinc oxide?
(*b*) What are the properties of zinc hydroxide?

6. (*a*) What are the uses for zinc chloride?
(*b*) What are the uses of zinc sulphate?
(*c*) What is lithopone and for what is it used?

7. Where is cadmium found?

8. How is cadmium used?

9. Name some of the compounds of cadmium.

10. (*a*) Where does mercury occur on the earth?
(*b*) How is mercury obtained from its sources?

11. (*a*) What are the properties of mercury?
(*b*) How are the uses of mercury related to its properties?

12. What are the properties of mercuric oxide?

13. Why does mercury appear monovalent in mercurous chloride?

14. What are the properties and uses of some mercuric salts?

15. How are the rare earths related?

16. What are the metals of Group VI of the periodic table?

17. (*a*) Where does chromium occur on the earth?
(*b*) How is chromium obtained from its oxide?

18. What are the properties of chromium?

19. How does uranium occur on the earth?

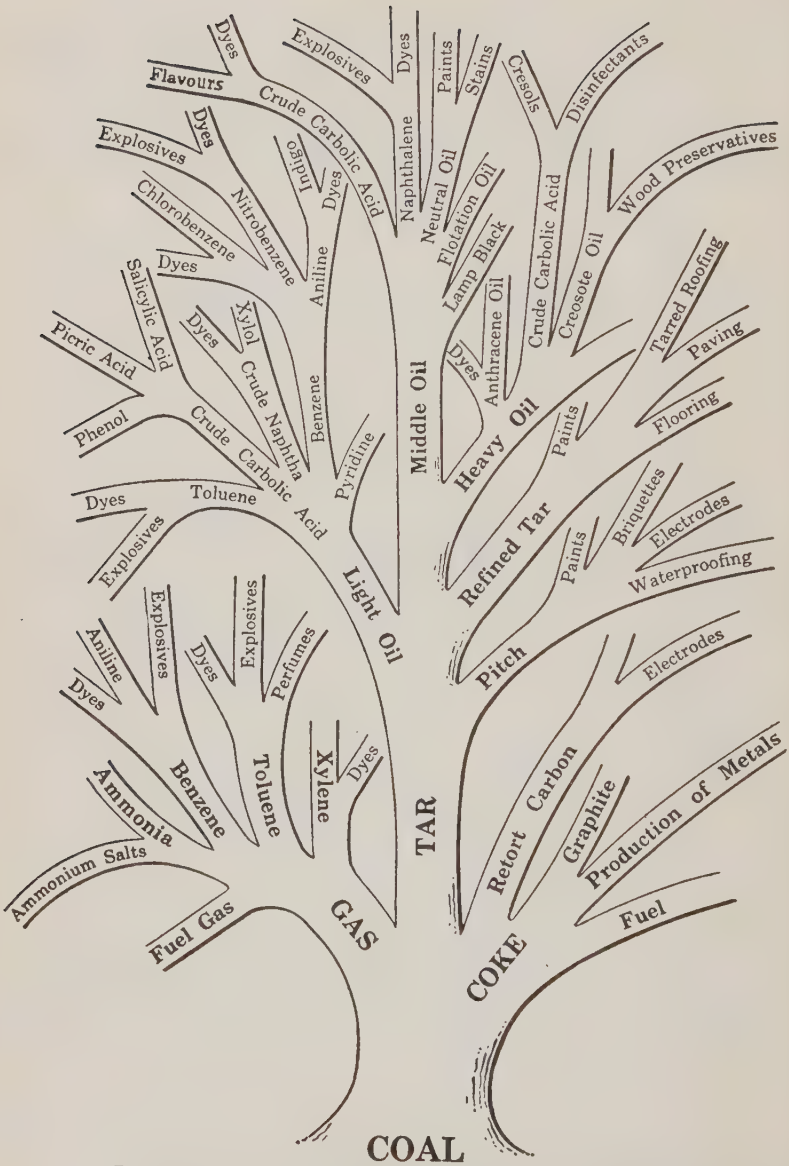
20. (*a*) What are the metals in Group VII of the periodic table?
(*b*) Where does manganese occur on the earth?
(*c*) How is manganese obtained from its ores?
(*d*) What are the two common alloys of manganese and iron? How are they obtained and for what are they used?
(*e*) What are the properties of manganese?

21. How does potassium permanganate react and for what is it used?

Topic Eight

THE MARVELS OF CARBON

While inorganic chemists and physicists were unfolding the story of the nature of the more abundant elements and their compounds the organic chemists were piecing together the puzzle of the compounds formed by living things. By 1831 Liebig had developed accurate methods of analyzing carbon compounds and his pupil Gerhardt was able to classify them into series having similar properties. He also established the existence of organic radicals and made possible the naming of the compounds. In 1858 Kekule observed that carbon nearly always has a valence of four even when it combines with itself. The identity and arrangement of the atoms and characteristic groups was slowly deduced by logical reasoning from painstaking and crucial experiments. The foundation was thus laid for determining the structure of the more than 300,000 carbon compounds. On this foundation the wonderful work of synthesizing dyes, drugs, perfumes, flavours, rubber, nylon and a host of other modern marvels has proceeded.



From Holmes: "Introductory College Chemistry," courtesy The Macmillan Company

Chapter 43

The Hydrocarbons

1. Introduction. An early study of the chemical substances known to man showed that they could be divided into two main groups. One group comprised those substances which were obtained from mineral material; while the other group included substances which were only obtainable from living matter. Since it was believed that the latter group of substances could have been formed only by means of the vital spark of life, they were termed *organic substances*, and their study formed the subject known as *organic chemistry*. The substances formed from material which was not connected with life were therefore called *inorganic*; their chemistry was known as *inorganic chemistry*.

In 1828 Wöhler prepared the organic substance *urea* from the inorganic substance *ammonium cyanate*. Urea was formerly obtainable only from urine and it was believed that a living organism was necessary for its production. Since ammonium cyanate was prepared from materials which were not in any way connected with a living being it was realized that organic chemistry did not depend upon living material. In a short time many organic compounds were prepared in the laboratory and it was found that such compounds follow the same natural laws in their formation as do inorganic substances. An examination of organic substances showed that they all contained the element carbon, so that the study of organic chemistry might be better termed the study of the compounds of carbon. For convenience the terms *inorganic* and *organic* are still used, but they no longer possess their early significance.

In earlier sections of this book we have studied the element carbon and some of its compounds, and we have seen that those compounds behaved in a similar manner to the other substances studied in inorganic chemistry. The organic compounds are found to consist of carbon, hydrogen, oxygen, nitrogen and a few other elements. Some of them, of course, do not contain all of these elements, and many of them consist of carbon and hydrogen alone. Many hundreds of thousands of organic substances have been prepared and identified.

From a utilitarian viewpoint the important property of most organic compounds is that they burn in oxygen, but a few like carbon tetrachloride which do not contain hydrogen are non-flammable. If an organic compound contains no elements other than carbon, hydrogen and oxygen it will burn completely to carbon dioxide and water.

$$C_7H_{16} \text{ (heptane)} + 11\ O_2 \longrightarrow 7\ CO_2 + 8\ H_2O$$

$$C_6H_{12}O_6 \text{ (glucose)} + 6\ O_2 \longrightarrow 6\ CO_2 + 6\ H_2O$$

$$2\ C_{57}H_{110}O_6 \text{ (stearin)} + 163\ O_2 \longrightarrow 114\ CO_2 + 110\ H_2O$$

The complete oxidation of the carbon and hydrogen part of any organic substance gives carbon dioxide and water but nitrogen, the oxides of nitrogen, sulphur dioxide, the oxides of phosphorus and other compounds may be formed, depending on the elements present in addition to hydrogen and carbon.

2. Hydrocarbons. Substances containing carbon and hydrogen only are known as *hydrocarbons*. Many of the properties of the hydrocarbons are found to be due to the unique property that carbon has of uniting with itself. Carbon atoms will join with one another so that they form long chains. In some cases the ends of the chains will join together and substances containing a "ring" of carbon atoms will be produced. The hydrocarbons that are built up in straight chains are known as *aliphatic* substances. The word "alipha-

tic" comes from the Greek word meaning fat, and is applied to the straight-chain hydrocarbons because they include most of the naturally occurring fats. The hydrocarbons containing a ring of carbon atoms are known as *aromatic* substances, since many of them have very aromatic odours. Although there are a large number of hydrocarbons, almost all of them may be placed in one of four series which may be represented by a type formula in which the number of carbon and hydrogen atoms may be represented by the letter "n". Each series is known as a *homologous* series and each member of the series is known as a *homolog*. The series are named from their first member, which has the lowest molecular weight, and each hydrocarbon differs from the preceding member of a series by the addition of one atom of carbon and two of hydrogen. The four series and their type formulas are given in Table 42.

TABLE 42—THE SERIES OF HYDROCARBONS

Methane series	C_nH_{2n+2}
Ethylene series	C_nH_{2n}
Acetylene series	C_nH_{2n-2}
Benzene series	C_nH_{2n-6}

3. The methane series. The members of this series of hydrocarbons are rather inert substances. They are often known by the name *paraffins*, which is derived from the Latin meaning "little affinity". They are also known as *alkanes*. The members of the series show an increase in their melting and boiling points, with increasing molecular weight. The more important members of this series are shown in Table 43. The first four members are gases, the next eleven are liquids, and the higher members are solids at ordinary temperatures. Since the valence bond between the carbon atoms consists of a single pair of electrons these hydrocarbons are known as *saturated*. Such hydrocarbons are found in petroleum and its products.

TABLE 43—THE METHANE SERIES OF HYDROCARBONS

Name	*Formula* (C_nH_{2n+2})	*M.P.* °C.	*B.P.* °C.
Methane	CH_4	−182.5	−161.4
Ethane	C_2H_6	−183.2	− 89.0
Propane	C_3H_8	−187.7	− 42.1
Normal Butane	C_4H_{10}	−138.3	− 0.5
Normal Pentane	C_5H_{12}	−129.7	36.0
Normal Hexane	C_6H_{14}	− 95.4	68.7
Normal Heptane	C_7H_{16}	− 90.6	98.4
Normal Octane	C_8H_{18}	− 56.9	125.6

The first member of the series is *methane*. This gas is produced by the bacterial decomposition of vegetable material under water. If a pool in a swamp is stirred by a stick, bubbles of gas will rise to the surface. This gas is methane and it may be collected in a bottle by displacement of water. Because of this common source of the gas it is sometimes called *marsh gas*. Natural gas and petroleum are formed from decayed vegetable and animal material, and they contain large amounts of methane. The gas is present in coal mines and collects in quantities that may be dangerous since it combines easily with oxygen and burns with a blue flame.

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$$

The gas is known to miners as *fire damp* and in the presence of a naked flame it will explode so its presence has been the cause of many disasters. The number of mine explosions was greatly reduced by the *Davy Safety Lamp*, which was invented by Sir Humphrey Davy. In this well-known lamp the flame is surrounded by a fine wire gauze which will allow a gas to enter and burn but will conduct heat away from the outside area of combustion so rapidly that the gas will not burn on

the outside of the gauze. If methane burns with an insufficient supply of oxygen, carbon monoxide is produced.

$$2\ CH_4 + 3\ O_2 \longrightarrow 2\ CO + 4\ H_2O$$

The presence of methane in mines may thus lead to the production of carbon monoxide which may cause suffocation and poisoning. Carbon monoxide is known to the miners as *after damp*.

Methane may be prepared in the laboratory by the reduction of carbon monoxide with hydrogen in the presence of a nickel catalyst.

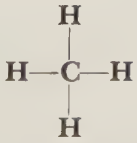
$$CO + 3\ H_2 \longrightarrow H_2O + CH_4$$

It may also be prepared by the reaction between aluminum carbide and water.

$$Al_4C_3 + 12\ H_2O \longrightarrow 4\ Al(OH)_3 + 3\ CH_4$$

Methane is a colourless gas which is slightly soluble in water. Although it burns easily it is not affected by vigorous oxidizing agents, such as nitric acid, potassium permanganate, or concentrated sulphuric acid. It combines directly with chlorine to form a series of substituted compounds.

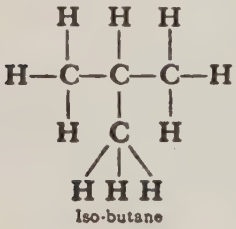
The formula of methane may be represented in two dimensions as follows, where straight lines represent the pairs of electrons.



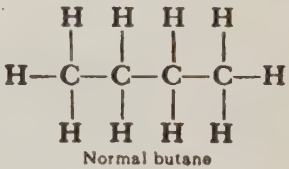
This is known as a structural formula, and is used frequently in organic chemistry to indicate the various radicals and atoms and the positions which they occupy with relation to one another.

The chief use of methane is as a fuel since it makes up over 80 per cent of natural gas and about one-third of coal gas. Since "carbon black" is produced by burning natural gas in a limited supply of air, methane is really its source. It has not been extensively used as a chemical raw material but some processes for using it to make methyl alcohol have been proposed. The higher members of the series are more useful.

4. Isomerism. It is possible to have two distinct butanes, which have the same molecular formula of C_4H_{10}, but have different properties. The existence of such substances, which have the same formula but a different arrangement of atoms, is known as *isomerism*. The substances themselves are known as *isomers*. The isomerism exhibited by butane is shown in structural formulas as,



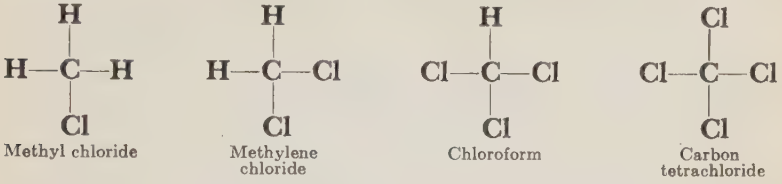
Iso-butane



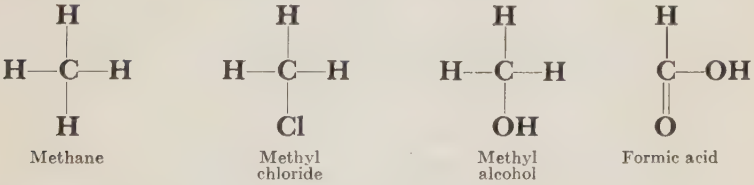
Normal butane

5. Substitution. An important property of the hydrocarbons is their ability to substitute various atoms or radicals for hydrogen atoms. This reaction produces *substitution products*, which may, in turn, undergo a further change in which the substituted atoms or radicals may be replaced by others. Methane reacts with chlorine in such a way that one atom of hydrogen is removed and one atom of chlorine is substituted for it. The substance produced is *methyl chloride*, or *chlormethane*, CH_3Cl. A further reaction with chlorine substitutes a second chlorine atom with the production of *methylene chloride*, or *dichlormethane*, CH_2Cl_2. A third chlorine atom produces *chloroform*, or *trichlormethane*, $CHCl_3$. Finally,

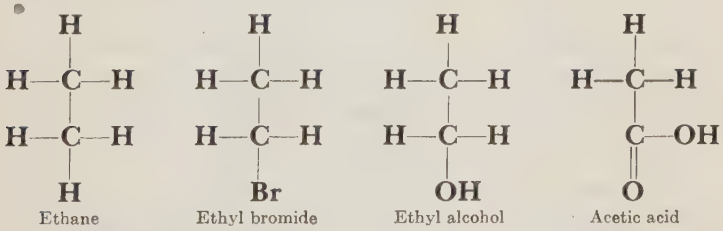
a fourth chlorine atom gives the completely substituted methane, *carbon tetrachloride*, or *tetrachlormethane*, CCl_4.



The idea of substitution is applied in thinking about all the derivatives of the hydrocarbons shown in the next chapter. Alcohols are thought of as hydrocarbons where the OH group replaces hydrogen on carbon and organic acids are formed when the hydrogen atoms are replaced by OH and O. Examples of such substitutions with methane are:



Similar substitutions with ethane give:



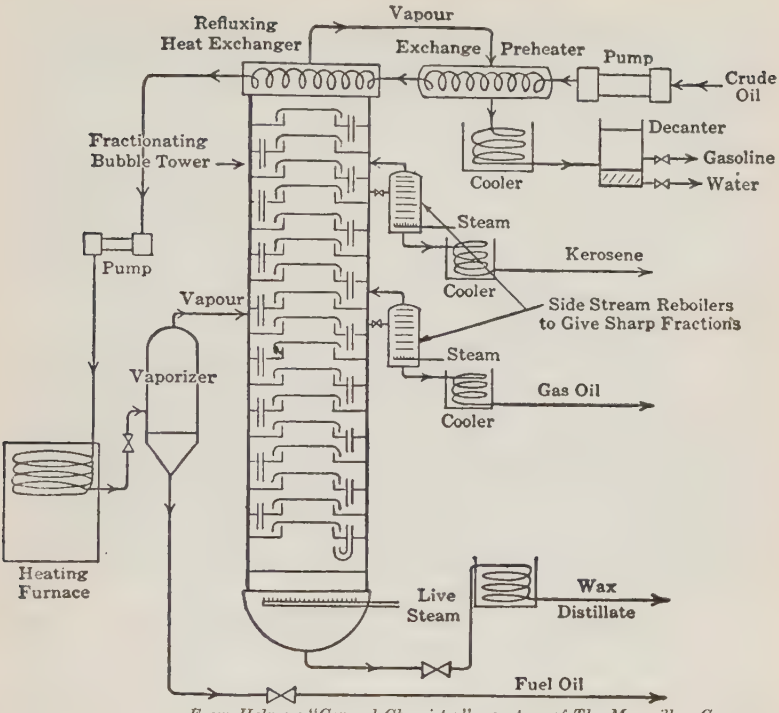
The COOH group is known as the carboxyl group and is characteristic of organic acids.

6. Natural gas is found in many parts of the world. As it is associated frequently with petroleum it is sometimes encountered when drilling for oil. As the gas consists largely of methane together with ethane, propane and small amounts of higher hydrocarbons, it is a good fuel. Most natural

gases contain some nitrogen and carbon dioxide, and sometimes these gases are present in sufficient quantities to prevent combustion.

7. Petroleum is a solution of gaseous and solid hydrocarbons in a mixture of liquid hydrocarbons. Most of the hydrocarbons are of the methane series, but petroleum from different parts of the world varies widely as to the nature of the hydrocarbons that it contains. Petroleum is found in certain rock formations accompanied by sand, and at depths varying from a few feet to over one mile. Wells are drilled into the oil-bearing strata and the oil is pumped to the surface. Some wells are so full of gas that the oil is forced to the surface without pumping and these are known as *gushers*. The name "petroleum" is derived from the Latin meaning "rock oil", and the crude and refined oil is known as *mineral oil* to distinguish it from oils of animal or vegetable origin. Petroleum was known to the American Indians who used it as a medicine.

8. Petroleum refining. The mixture of hydrocarbons consists of compounds whose boiling points are very close together. No attempt is made to separate the individual hydrocarbons from the mixture but they are separated into groups boiling between certain ranges of temperature. The process of separating them into such fractions is called *fractional distillation*. It is done by having a series of plates or pans one above the other so arranged that the vapour from the lower plate heats the liquid on the plate above. The liquid on the plate above is cooler than the vapour which passes through it so the higher boiling constituents condense and the more volatile ones pass up to another plate. Gasoline vapour passes through the tower, kerosene condenses in the upper portion, gas oil in the middle, and heavier oils at the bottom. The heavier oils are steam-distilled and divided into several portions. Solid paraffin is removed from these oils by cooling, and coloured impurities are removed by fuller's earth.



From Holmes: "General Chemistry", courtesy of The Macmillan Company

Fig. 228. The various products are separated from petroleum by fractional distillation.

Sulphur compounds are removed from petroleum products by washing with sulphuric acid or lye. Gums and waxes are removed from motor oils by treatment with a solvent, such as liquid sulphur dioxide. The residue contains tar and coke.

Petroleum ether, *benzine*, or *naphtha*, is the fraction boiling between 36°C. and 100°C. It is used as a solvent and as a dry-cleaning fluid. *Gasoline* is the fraction boiling between 100°C. and 200°C. *Kerosene* boils between 200°C. and 300°C. It is used for illumination purposes and as a fuel oil for stoves. Before the introduction of the automobile, it was one of the most valuable products of petroleum refining. *Gas oil* boils up to 375°C. It is used as a fuel, for enriching water gas,

and for cracking. *Lubricating oil* contains higher members of the hydrocarbons and is used for lubrication. *Vaseline* is a semi-solid and is used in medicine and for lubrication. *Paraffin* is a solid melting at about 60°C. and is used for waterproofing and for making candles. *Tar* is used in the manufacture of asphalt. *Petroleum coke* is used as a fuel and in the manufacture of electrodes. *Liquid petrolatum* consists of highly refined high-boiling hydrocarbons and is used in medicine.

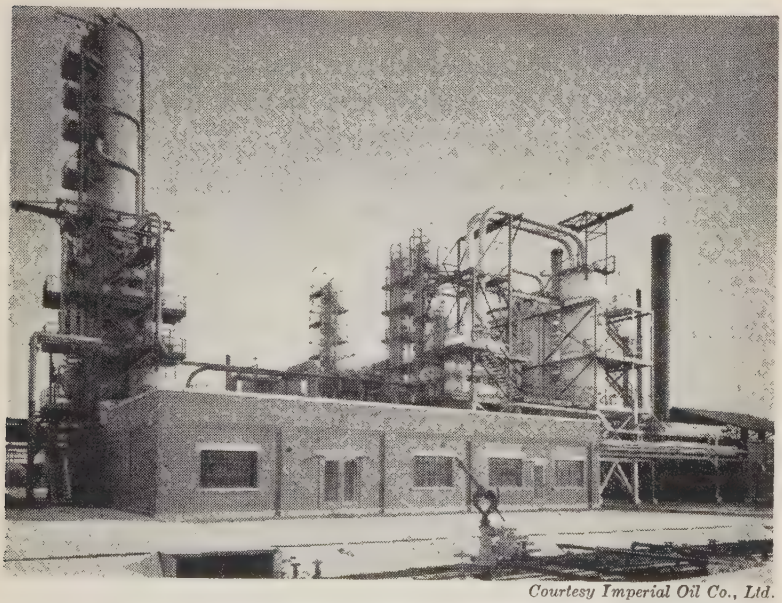
9. Gasoline consists of a mixture of hexane, heptane, octane and nonane. Because of the large numbers of internal combustion engines in use, the production of gasoline has become one of the most important industries. The natural gasoline fraction in petroleum is about 20 per cent, but modern refining practice has raised this to over 40 per cent. A large part of the increase in gasoline production is due to *cracking*, a process developed by Burton in 1913. It consists of the breaking up of heavy hydrocarbons into lighter ones under the influence of heat, pressure, and, sometimes, a catalyst. Examples of cracking are given by the following reactions.

$$C_{12}H_{26} \longrightarrow C_6H_{14} + C_5H_{12} + C$$

$$C_{12}H_{26} \longrightarrow C_6H_{14} + C_6H_{12}$$

After cracking, the oil passes into a flash chamber and then through a bubble tower. The cracking process provides about half of the gasoline supply, and also produces lighter hydrocarbons which are suitable as fuel for aircraft.

Some of the gasoline is produced by *polymerization* which is the combination of molecules of light hydrocarbons to form molecules of heavier ones. This is done by employing high temperatures and pressures with suitable catalysts. Sometimes heavy hydrocarbons are cracked to form lighter ones, which are then polymerized to form other hydrocarbons more suitable for use in gasoline.



Courtesy Imperial Oil Co., Ltd.

Fig. 229. A cracking unit (left), a polymerization unit and a clay-treating unit at a Western Canadian oil refinery.

Natural gas contains, besides methane, the vapours of low-boiling hydrocarbons. These can be recovered by absorption with activated charcoal, by washing the gas with an oil in which they are soluble, or by condensing and cooling the gas to cause them to liquefy. This type of gasoline is known as *casing-head gasoline*.

Since the power obtained from the explosion of gasoline vapour in the cylinders of an internal combustion engine depends upon the expansion at the time of the explosion, compression of the gas before the explosion will increase the power. For this reason modern engines use a high compression ratio. This results in increased power, but ordinary gasoline produces an objectionable "knock". This knock is the result of a sudden explosion in the cylinder, and it may be reduced by developing a slower push against the piston. To reduce knocking, gasoline is blended by using various pro-

portions of hydrocarbons produced by straight distillation, cracking, polymerization, or from natural gas.

Gasoline is given a rating, known as the *octane number*, with regard to its tendency to produce knocking in a standard test engine. A hydrocarbon known as 2,2,4-trimethylpentane does not produce a knock and is given a rating of 100. Normal heptane produces a pronounced knocking, and is given a rating of 0. To obtain a rating for a particular blend of gasoline, it is used in the standard engine, and its tendency to knock is compared with a mixture of 2,2,4-trimethylpentane and heptane. If the gasoline produces the same intensity of knocking as a mixture containing 88 per cent of 2,2,4-trimethylpentane, it is given an octane number of 88.

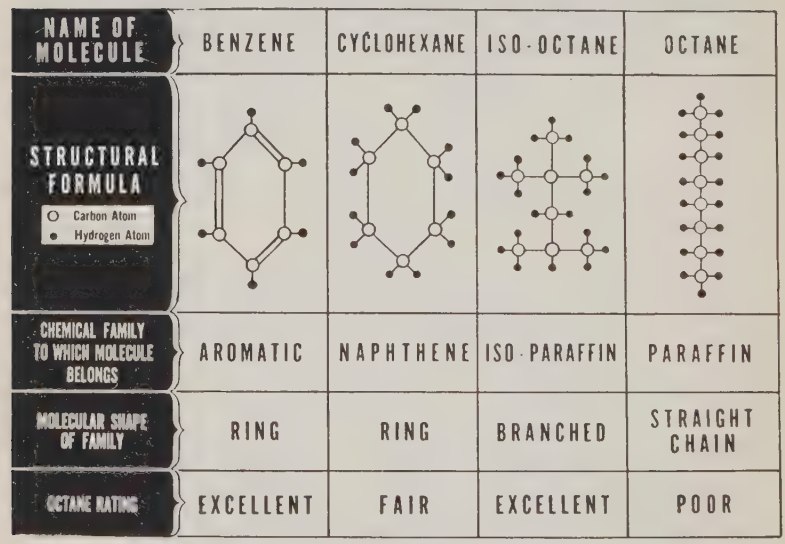


Fig. 230. Some hydrocarbons cause more "knocking" in an engine than others.

10. The ethylene series. The members of this series differ markedly from the paraffins. They are known as the *olefins* and they are more active than the paraffins. The first member of the series is *ethene* or *ethylene*. This hydrocarbon

will react readily with two atoms of chlorine to form *ethylene dichloride*, and it is found that these two chlorine atoms are attached to different carbon atoms. An examination of the reactions of ethylene shows that its two carbon atoms must share two pairs of electrons. This form of linkage may be represented in a structural formula by two lines, and is known as a *double bond*. Compounds containing a double bond are said to be *unsaturated*.

Ethylene is used to hasten the ripening of citrus fruits. The green-coloured fruit is exposed to an atmosphere containing a small quantity of the gas, and it soon reaches the colour of ripened fruit.

11. The acetylene series. This series consists of hydrocarbons which show a greater activity than the olefins. They are usually named after *acetylene*, the first member, but they are sometimes known as the *alkynes*. Some of the members of the series are shown in Table 44.

TABLE 44—THE ACETYLENE SERIES OF HYDROCARBONS

Name	*Formula* (C_nH_{2n-2})	*M.P.* °C.	*B.P.* °C.
Acetylene	C_2H_2	− 81.0	−83.6
Propyne	C_3H_4	−102.7	−23.2
Butyne	C_4H_6	−122.5	8.6
Pentyne	C_5H_8	− 98.0	39.7

The acetylene molecule possesses a *triple bond* due to the sharing of three pairs of electrons by the two carbon atoms and may be represented by H—C ≡ C—H. It is a poisonous gas which burns with a smoky flame and is very explosive (see Chap. 33, sec. 13). The gas is more explosive when it is compressed, but it may be dissolved under 12 atmospheres pressure in acetone which is held in steel tanks filled with "kapok". The oxy-acetylene torch, used widely for welding

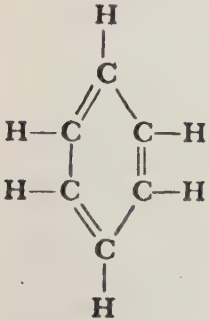
and cutting metals, was described in Chapter 5. Large amounts of acetylene are produced in Canada as its addition products are used for the synthesis of many organic compounds. It is the basis of a large synthetic chemical industry at Shawinigan Falls, Quebec.

Courtesy Shawinigan Chemicals Ltd.

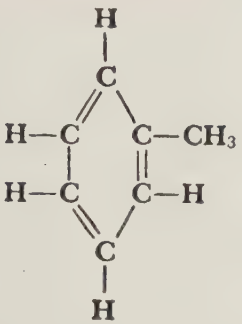
Fig. 231. Aerial view of the plants which make chemicals from acetylene. The carbide furnaces can be seen in the background.

12. The benzene series. The members of this series are known as the *aromatic* hydrocarbons because they and many of their compounds possess an aromatic odour. The first three members of the series are among the hydrocarbons obtained from coal tar, and they differ widely from those found in petroleum and natural gas. They form substitution products quite readily, and the higher members of the series are derived from benzene by substituting a CH_3 radical for one of the hydrogen atoms. The replacement of one hydro-

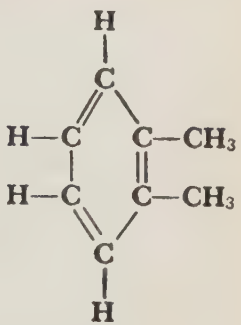
gen atom in benzene gives toluene. A similar replacement in toluene gives xylene.



Benzene

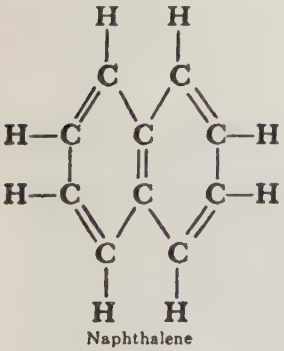


Toluene

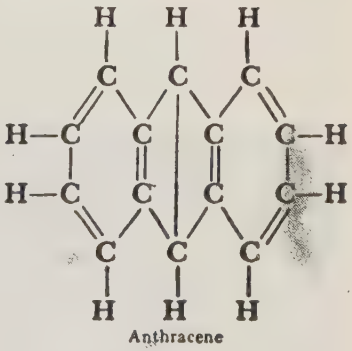


Xylene

13. Naphthalene and anthracene. Coal tar is also the source of two other important hydrocarbons, *naphthalene* and *anthracene*. These hydrocarbons contain two and three rings respectively and are related to the benzene series. Their structural formulas are shown as:



Naphthalene



Anthracene

Naphthalene is used in the manufacture of *moth balls*, in the enrichment of water gas, and in the manufacture of many organic compounds, including several dyes. Anthracene is used in the manufacture of many important dyes.

14. Rubber is formed by the coagulation of the juice of certain trees and shrubs, the principal source being the tree *Hevea brasiliensis*. The trees are tapped by cutting through

the bark, and the juice, which is known as *latex*, is collected in cups. Latex is an emulsion of rubber particles dispersed in water and may be coagulated by acetic acid. In the production of rubber from wild trees by the natives, wooden paddles are dipped into the latex and held in wood smoke from a fire. When the acetic acid in the smoke has coagulated the latex the paddles are dipped again. This is repeated until a large ball of rubber accumulates on the end of the paddle. The emulsion of latex may be preserved and used in industry for making cord tires and dipped articles such as gloves. The particles of latex have a negative charge, and it is possible to deposit them by an electric current and build up a rubber deposit on forms.

Pure rubber is brittle in winter and sticky in summer, and, for a long time, this property prevented it from being made into useful articles. This difficulty was overcome by the discovery of vulcanization which has been discussed during the study of sulphur (see Chap. 14, sec. 6). Several substances are added to rubber in addition to sulphur. These fillers increase the strength, toughness and resistance to wear of the

Courtesy Dominion Rubber Co., Ltd.

Fig. 232. Natural rubber piled up in an Eastern Canadian warehouse.

finished product, besides producing a colour. Antimony sulphide, carbon black, zinc oxide and barium sulphate are among the many fillers used.

In the last few years a large number of synthetic rubbers have been produced. These are not varieties of real rubber that have been made from different materials, but are rubber-like substances which can be used for the same purposes as natural rubber. In some cases the synthetic product is better in certain respects than the article produced from natural rubber.

Some of the synthetic rubbers fall into the class of the plastics and will be mentioned in a later chapter. They have many uses, and, in some respects, are far better than the natural product. Canada has developed a large synthetic rubber industry at Sarnia, Ontario.

Question Summary

1. (*a*) What was the early distinction between inorganic and organic chemistry?

(*b*) What was the experiment of Wöhler and how did it lead to the modern definition of organic chemistry?

2. Define: aliphatic, aromatic, homologous series.

3. (*a*) What is the general formula for the methane series? Write the formulas for the first six members of the series.

(*b*) What is the principle of the Davy safety lamp?

(*c*) How do you account for the presence in mines of fire damp and after damp?

(*d*) How is methane prepared in the laboratory?

(*e*) What is the chief use of methane?

4. Explain isomerism and illustrate by the isomers of butane.

5. Write the formulas for the substitution products of methane.

6. What is natural gas?

7. Describe the occurrence of petroleum.

8. (*a*) Describe the refining of petroleum by fractional distillation.

(*b*) Give the products obtained during petroleum refining.

9. (*a*) What is the composition of gasoline? How is gasoline produced by cracking?

(*b*) How is gasoline produced by polymerization? What is meant by casing-head gasoline?

(*c*) Explain what is meant by the octane number of gasoline.

10. What is meant by unsaturated compounds?

11. What are the properties and uses of acetylene?

12. (*a*) Write the structural formulas for the first three members of the benzene series.

(*b*) What are the properties of the hydrocarbons of the benzene series and what types of compounds do they form?

13. Describe naphthalene and anthracene.

14. (*a*) Describe the production of natural rubber.

(*b*) Describe the preparation of rubber articles (*Encyclopedia*).

(*c*) Discuss the production of synthetic rubber.

Chapter **44**

The Relatives of the Hydrocarbons

1. Introduction. Many substances may be obtained by the substitution of different atoms or radicals in various organic compounds. These substances are known as the *derivatives* of the hydrocarbons. The residue of the hydrocarbon from which the substances have been derived is known as the *alkyl* or *aromatic radical*, and may be designated by the letter "R" in a type formula which indicates clearly how the derivative is built. We shall discuss briefly a few of the common types of derivatives and the more important compounds of each type.

2. The alcohols. The alcohols are organic substances which contain the OH radical and have the type formula R—OH. Although they possess the OH radical, they are not hydroxides since they do not dissociate in water to form hydroxyl ions. They may be considered as being derived from the hydrocarbons by the substitution of the OH radical for a hydrogen atom, so there will be a series of alcohols corresponding to each series of hydrocarbons.

The best-known alcohols are the first two in the series which is derived from the methane hydrocarbons. They are methyl and ethyl alcohol, which are derived from methane and ethane respectively. Only one structural formula is possible for each of these two alcohols.

Methyl alcohol	CH_3OH
Ethyl alcohol	CH_3CH_2OH

3. Methyl alcohol, or *methanol*, CH_3OH, used to be prepared almost entirely by the destructive distillation of wood

and was known as *wood alcohol*. The wood was heated in retorts in the absence of air. Acetic acid, acetone, methanol and tar were produced in the distillate, which was known as *pyroligneous acid*. About two gallons of alcohol were obtained from a ton of wood.

Methanol can also be obtained by the combination of hydrogen and carbon monoxide in the presence of a catalyst.

$$CO + 2\ H_2 \longrightarrow CH_3OH$$

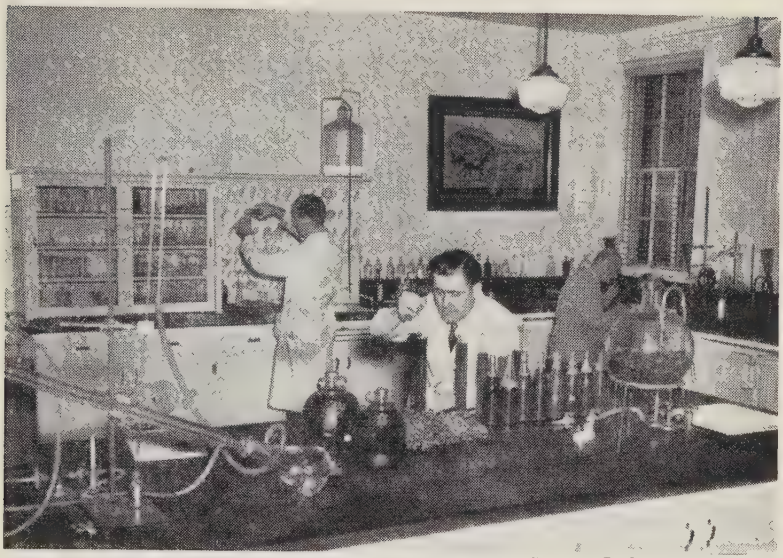
This process was developed in Germany, and can produce methyl alcohol so cheaply that it must eventually supplant the wood distillation process entirely.

Methanol is a colourless liquid boiling at 65°C. It is poisonous when taken internally or when its vapour is breathed. It acts on the optic nerve to produce permanent blindness, and it may cause death owing to the products of its oxidation within the body. It must not be confused with ethyl alcohol which is used in alcoholic beverages. The name "methanol" is now used almost exclusively in order to avoid the use of the word "alcohol", and thus prevent the substance from being consumed in error or in ignorance of its danger.

Methanol is used extensively in an anti-freeze for automobile radiators, and as a solvent in many industrial processes. It is also used as a denaturant for ethyl alcohol to make it unfit for human consumption.

4. Ethyl alcohol, or *ethanol*, C_2H_5OH, has been known to man for many years, and early historical references have been made to its preparation by distillation and to its use in beverages. Simple distillation is one of the oldest known chemical processes.

Ethanol is prepared usually by the alcoholic fermentation of sugars through the action of yeast. *Fermentation* is a chemical change brought about by the action of microscopic



Courtesy Jordan Wine Co., Ltd.

Fig. 233. Ethyl alcohol is produced when sugars ferment with yeast.

organisms. The souring of milk and the production of vinegar from cider are examples of *acid fermentation.* The starting point of alcoholic fermentation is either the sugar *glucose*, $C_6H_{12}O_6$, or substances which may be converted into glucose or similar sugars. The reaction consists of the production of ethanol and carbon dioxide.

$$C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH + 2\ CO_2$$

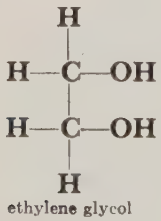
Fermentation will proceed until the alcohol which is produced reaches a strength of about 17 per cent. A higher concentration of alcohol will kill the yeast cells. Only a 95 per cent alcohol solution may be obtained by fractionally distilling the water-alcohol mixture. The remaining water must be removed by chemical means. Pure alcohol which does not contain any water is known as *absolute alcohol.*

Ethanol is a colourless liquid which mixes with water in all proportions. It is, next to water, the most widely used solvent, and it has many industrial applications. It is used

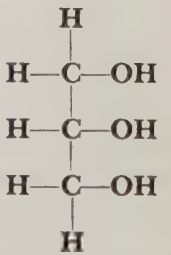
in the preparation of numerous organic compounds, in medicine and as an anti-freeze. Ethanol may be used as a fuel, but it is not as satisfactory as gasoline. "Canned heat" is solidified alcohol made from ethanol and soap.

Ethyl alcohol has been used in beverages for many years. When taken into the body, it is absorbed from the stomach and passes directly into the blood. A small proportion is used as a food, but the quantity is not large. It tends to increase the heart action and may be believed to be a stimulant, but the effect does not last and may be followed by a feeling of depression. The products of the oxidation of alcohol in the body are carbon dioxide and water which are themselves harmless, but the danger of alcohol is its effect on the nervous system and other body organs.

5. Glycol and glycerol. If the two hydrogen atoms on different carbon atoms are each replaced by OH we call the products *glycols* or di-hydroxy alcohols. If three hydrogen atoms on different carbon atoms are replaced by OH then the substances are *glycerols* or tri-hydroxy alcohols. The structural formulas of the best known ones are given below with their names.



ethylene glycol



glycerine or glycerol

Ethylene glycol is a colourless liquid which looks like thin sugar syrup. It is used as an anti-freeze in automobile radiators instead of methanol or ethanol because of its higher boiling point, 197°C., which causes water to be

evaporated off more rapidly than the anti-freeze It is said to be toxic when taken internally and it has a sweet taste like glycerine.

Glycerine is a more syrupy liquid than glycol, with a still higher boiling point, but it chars and decomposes when strongly heated and is less suitable for an anti-freeze. It is miscible with water in all proportions and is very hygroscopic. It is added to tobacco products to prevent drying, and it is utilized in medicines and confections. Most of it is used to make nitro-glycerine for dynamite and to prepare hand lotions.

If glycerine is dropped slowly into a mixture of concentrated sulphuric acid and fuming nitric acid, which is kept below 20°C., the trinitrate $C_3H_5(NO_3)_3$ is produced. This compound is known as *trinitroglycerine*. In the formation of these compounds it will be seen that each NO_3 radical

Courtesy Canadian Industries Ltd.

Fig. 234. Explosives are used to move vast quantities of rock and earth.

replaces one of the OH radicals and not one of the hydrogen atoms. In the above nitration, the sulphuric acid acts as a dehydrating agent by uniting with the water, which is produced by the reaction, thus preventing the dilution of the nitric acid.

Nitroglycerine is a heavy oily liquid with a sweet taste, and is usually a pale yellow colour. It is very sensitive to shock and can be detonated by a sharp blow. To reduce its sensibility to shock it may be mixed with diatomaceous earth, clay, wood pulp, or sawdust, in which form it is known as *dynamite*. *Blasting gelatine* is made by dissolving nitrocellulose in nitroglycerine. Smokeless powders such as *cordite* are made with nitroglycerine, nitrocellulose, vaseline and acetone.

6. Ethers. When two molecules of methyl alcohol are dehydrated by heating with sulphuric acid, they will become linked by an oxygen atom to form *dimethyl ether*. The ethers correspond to the oxides of inorganic chemistry. If alcohol is considered as water in which one hydrogen atom has been replaced by an organic radical, an ether may be thought of as water which has had both its hydrogen atoms replaced by organic radicals.

$H—O—H$	$CH_3—OH$	$CH_3—O—CH_3$
Water	Methyl alcohol	Dimethyl ether

Diethyl ether, commonly known as *ether*, $C_2H_5OC_2H_5$, is the best known of the ethers. It is a colourless liquid with a boiling point of 35°C. It is very flammable and great care must be taken to avoid fires when it is used. It must never be distilled or heated over an open flame, and it is better to use electric heaters. Ether was first used as an anesthetic by Morton in 1846, and it is still used for that purpose.

7. Aldehydes. When primary alcohols are oxidized at a low temperature, so as not to produce complete combustion,

compounds known as *aldehydes* are formed. The two most important aldehydes are *formaldehyde* and *acetaldehyde*. When oxidized, aldehydes produce organic acids, and these substances form formic and acetic acids respectively.

Formaldehyde, HCHO, is produced from methyl alcohol. It is a gas, but it is commonly known in the form of its 40 per cent solution in water, which is known as *formalin*. Formalin is used as a disinfectant, a spore killer and as a tissue preservative.

8. Acids. When aldehydes are oxidized they produce compounds having the formula R—COOH. The COOH radical is known as the *carboxyl* radical. When dissolved in water, the hydrogen atom of the carboxyl radical will dissociate to form a hydrogen ion, so these substances are acids. The acids are carboxyl derivatives of the hydrocarbons. Those containing one carboxyl radical and being derived from the methane series of hydrocarbons are known as *fatty* acids. Many organic acids occur in nature, either free, or in the form of salts and other compounds.

The first acid of the fatty acid series is *formic* acid, HCOOH, which occurs in nature in nettles, bees and ants. It derives its name from the Latin for ant. The irritation caused by the sting of certain insects is due to the injection of formic acid. Formic acid is a colourless liquid boiling at 101°C. and having a pungent odour. It may be prepared by the direct oxidation of methyl alcohol.

$$CH_3OH + O_2 \longrightarrow H_2O + HCOOH$$

or by the oxidation of formaldehyde,

$$HCHO + (O) \longrightarrow HCOOH$$

The second member of the fatty acid series is *acetic acid*, CH_3COOH, which can be obtained by the distillation of wood. The *pyroligneous acid* obtained from the distillation is

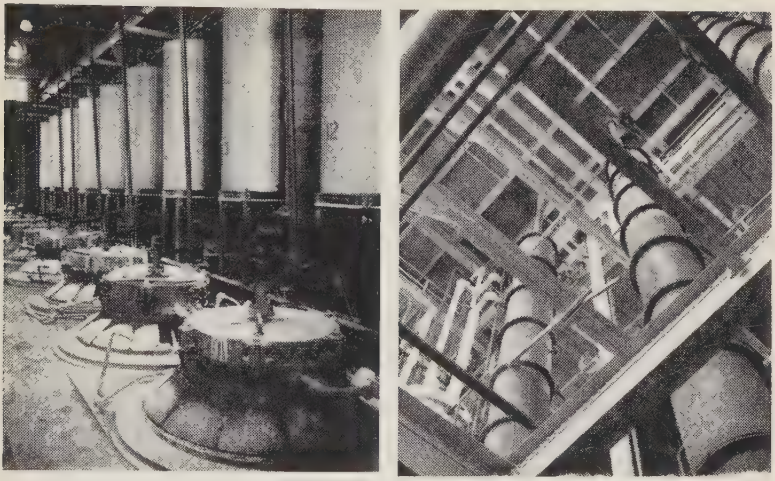
treated with lime which converts the acetic acid into calcium acetate. This is recovered by evaporation to dryness and treated with sulphuric acid. On distillation of the mixture the volatile acetic acid is obtained. Acetic acid can also be obtained from ethyl alcohol by oxidation. If fruit juices such as cider be allowed to ferment, alcohol will be produced with the formation of *hard cider*. The hard cider is then treated with the micro-organisms which bring about the change to acetic acid. These bacteria are known as *mother of vinegar*. The process is slow, but it may be speeded up by circulating the solution containing the alcohol through beechwood shavings soaked with mother of vinegar. This process gives *cider vinegar*; this contains about 5 per cent of acetic acid and has a brown colour. Colourless *white wine vinegar* is prepared by the action of the micro-organisms on alcoholic solutions or by the dilution of synthetic acetic acid with water.

The more important higher members of the fatty acid series are as follows:

Propionic acid	CH_3-CH_2-COOH
Butyric acid	CH_3-$(CH_2)_2$-COOH
Palmitic acid	CH_3-$(CH_2)_{14}$-COOH
Stearic acid	CH_3-$(CH_2)_{16}$-COOH

The last two acids are found in the animal fat *stearin*. Peanut oil contains *oleic acid*, $CH_3(CH_2)_6-CH=CH-(CH_2)_7-COOH$, which is unsaturated. *Lactic acid*, $CH_3-CHOH-COOH$, contains an OH radical and is an example of a hydroxy acid. It is produced in the souring of milk by the action of bacteria on milk sugar.

Oxalic acid, $COOH-COOH$, is a dibasic acid which contains two carboxyl radicals. It is found in certain sour plants in the form of its acid potassium salt. It is a fairly strong acid, and is used as an ink remover and as a bleaching agent for straw and leather. It is a poison.



Courtesy Shawinigan Chemicals Ltd.

Fig. 235. Acetic acid from acetylene is used to make other organic chemicals in these jacketed kettles and stills.

Tartaric acid is an important dibasic acid prepared from crude tartar, which is found in the containers in which wine or grape juice has been stored. Its structural formula may be represented by $COOH-CHOH-CHOH-COOH$. In addition to being a dibasic acid it is also a di-hydroxy acid. Some of its important salts have been mentioned, *cream of tartar*, $KHC_4H_4O_6$, *tartar emetic*, $KSbOC_4H_4O_6$, and *rochelle salts*, $KNaC_4H_4O_6$. Crystals of the last salt are easily melted but they are used in the manufacture of oscillators for ultra-sonic waves, for microphones, and for other places where sound waves are converted to electrical impulses.

Citric acid, $COOH-CH_2-COH(COOH)-CH_2-COOH$, is a tribasic acid which is present in the juices of citrus fruits. The acid is used in beverages, and the magnesium salt is used often in medicine.

Salicylic acid, $C_6H_4OHCOOH$, is a hydroxy aromatic acid occurring in oil of wintergreen. Both the acid and its ester, *methyl salicylate*, $C_6H_4OHCOOCH_3$, have antiseptic and analgesic properties. The acid reacts with acetic anhydride

to form *acetylsalicylic acid*, $C_6H_4OCOCH_3COOH$, which is known by trade names such as aspirin.

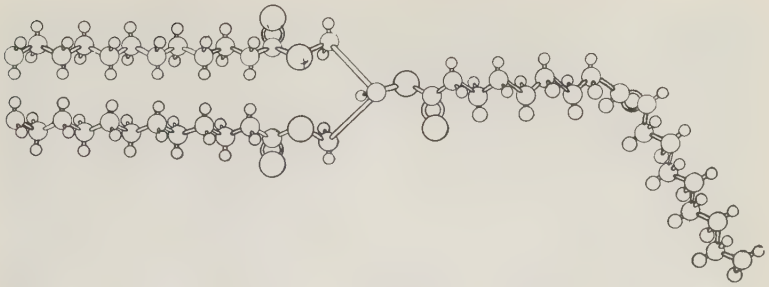
9. Esters. Esters are compounds in which the hydrogen of a carboxyl radical is replaced by an organic radical. This is done by the reaction between the acid and an alcohol, in which the alcohol is analogous to a base, and the ester to a salt. The esters are not salts since they do not dissociate to form ions. The production of esters is known as *esterification*, and the reaction proceeds slowly to an equilibrium. It thus differs from neutralization which proceeds very rapidly. Esters have a tendency to hydrolyze in the presence of water and this reaction is the reverse of esterification. To prevent this reverse reaction from taking place the preparation of esters is carried out in the presence of a substance which will absorb the water as soon as it is formed. This will disturb the equilibrium and the reaction can then proceed to completion.

With organic acids, alcohols form esters with the type formula R—COOR, as for example the production of ethyl acetate from ethyl alcohol and acetic acid.

$$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$$

Most of the esters have fragrant odours and are used as flavouring extracts. *Isoamyl acetate*, $CH_3COOC_5H_{11}$, has the odour of pears; *methyl butyrate*, $C_3H_7COOCH_3$, has the odour of pineapples; *isoamyl isovalerate*, $C_3H_7COOC_5H_{11}$, has the odour of apples; and *octyl acetate*, $CH_3COOC_8H_{17}$, has the odour of oranges.

10. Soaps. The salts of the fatty acids are known as *soaps*. Those used for washing purposes are the sodium or potassium salts but the soaps of the heavier metals have various commercial uses. Ordinary soap is made by hydrolzing the natural fats with sodium or potassium hydroxide. The natural fats, such as *palmitin*, *stearin* or *olein*, are the tri-



Courtesy Procter and Gamble Co.

Fig. 236. A fat molecule that can be used in soap making.

esters composed of glycerine and the fatty acids, and their hydrolysis in the presence of the alkali produces glycerine and the soap. This is shown by the action of sodium hydroxide on stearin.

$$\begin{array}{l} H_2C{-}O{-}O{-}C{-}C_{17}H_{35} \\ H{-}C{-}O{-}O{-}C{-}C_{17}H_{35} \\ H_2C{-}O{-}O{-}C{-}C_{17}H_{35} \end{array} + 3\,NaOH \rightarrow \begin{array}{l} H_2{-}C{-}OH \\ H{-}C{-}OH \\ H_2{-}C{-}OH \end{array} + 3\,NaOOC{-}C_{17}H_{35}$$

stearin — glycerine — soap

Sodium hydroxide produces a *hard soap*, while potassium hydroxide gives a jelly-like mass known as *soft soap*.

White soaps are usually made from tallow, palm oil, or cocoanut oil, while laundry soaps are made from tallow, bone grease, or cotton-seed oil. The fat is heated with live steam and sodium hydroxide is added to bring about the hydrolysis. Sodium chloride is added to separate a portion of the soap which is not soluble in brine and lye, and later more salt is added. The soap forms an upper layer floating on a layer of sodium hydroxide, salt and glycerine solution, which is drawn off and processed to give glycerine. The soap is treated with more alkali to complete the saponification, and is then kneaded to obtain a uniform composition. During the kneading fillers and perfumes are added. The soap is allowed to dry and harden and is then cut into bars. After the bars have hardened further they may be moulded into cakes. Sometimes the bars are chipped and dried quickly, and the chips milled and pressed into cakes. Various materials are added depending on the type of soap. Transparent soaps contain alcohol and glycerine. They may be made by dissolving soap in alcohol and distilling off the alcohol until a jelly-like mass is obtained, which may be moulded into cakes. Floating soaps may be made by beating air into the soap during the milling operation. Some scouring soaps contain sodium carbonate, borax, sodium silicate, or sand. Medicinal effects

Courtesy Procter and Gamble Co.

Fig. 237. Perfume and other materials are added in this soap crutcher.

are obtained by the addition of camphor, thymol, phenol, zinc oxide, etc. Dyes are added to give the required colour. Soaps form a colloidal suspension in water and their cleansing action has already been mentioned (Chap. 26, sec. 16).

11. Hydrogenation. Unsaturated substances usually have lower melting points than those which have only single bonds. It has been found that they will take up hydrogen at the double bond and become saturated compounds. This process is known as *hydrogenation*, and it is used frequently to raise the boiling point of oils which are to be used for cooking, the manufacture of hard soap, shortening or margarine. If an unsaturated vegetable oil is heated with hydrogen under pressure in the presence of finely divided nickel as a catalyst, a semi-solid material will be formed. Domestic shortening and other lard substitutes are made in this way. The hydrogenation is only carried to a point where the substance is suitable for its intended use, as complete hydrogenation

would produce a hard brittle solid. The catalyst is filtered out while the oil is hot. It is possible to produce tasteless edible solids from oils which could not be used otherwise.

One of the most abundant unsaturated fats is olein, $C_3H_5(C_{17}H_{33}COO)_3$. This occurs in a great many vegetable and animal oils. It takes up hydrogen at the double bonds to form stearin which is abundant in tallow. The product of the hydrogenation of *olein* was the first fat to be used as a butter substitute so the product was called oleomargarine. The "oleo" part of the name has now been dropped.

Margarine, which is used in almost all countries as a butter substitute, may be prepared by mixing a hydrogenated oil with vegetable fats, and churning with milk or cream. In some cases a small amount of butter is used. The product is colourless but it may be coloured by a vegetable dye. It has a good food value, and the better grades can hardly be distinguished from butter.

Question Summary

1. What is meant by substitution in organic chemistry?

2. (*a*) Write the type formula for an alcohol. Why are they not considered as bases?
   (*b*) Write structural formulas for two alcohols.

3. (*a*) How is methyl alcohol prepared? What is pyroligneous acid?
   (*b*) What are the properties and uses of methyl alcohol?

4. (*a*) Describe alcoholic fermentation.
   (*b*) What is absolute alcohol and how is it prepared?
   (*c*) What are the properties of ethyl alcohol?

5. (*a*) What is glycol and for what is it used?
   (*b*) What is glycerine and how is it made?
   (*c*) Describe the action of nitric acid on glycerine, and give the uses of the products.

6. (*a*) Write the formulas of two ethers.
   (*b*) What are the properties and uses of ethyl ether?

7. Write the type formula for an aldehyde. What are the properties and uses of formaldehyde?

8. (*a*) What is the type formula of an acid? What are the properties of formic acid?
(*b*) What are the properties and uses of acetic acid?
(*c*) How is vinegar produced?
(*d*) Name an aromatic acid and give its use.

9. (*a*) What is meant by esterification?
(*b*) Give the properties of some of the esters.

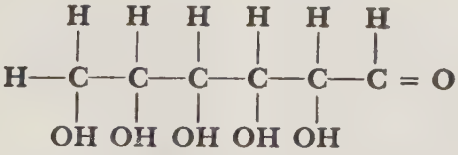
10. (*a*) Write the equation to show the production of a soap.
(*b*) Describe the method of making soap.

11. (*a*) Explain the principle of hydrogenation.
(*b*) How is hydrogenation carried out?
(*c*) Describe the production of margarine.

Chapter **45**

Carbohydrates and Proteins

1. Carbohydrates. You know that the three chemical forms of food are the fats, carbohydrates and proteins. You have just learned that the fats are esters of glycerine and the fatty acids and you can guess from the name that the carbohydrates are of the same composition as if they were hydrates of carbon. The formula of sucrose is $C_{12}H_{22}O_{11}$ and of glucose $C_6H_{12}O_6$. The carbohydrates have OH and H on either side of almost every carbon atom so they are not true hydrates. The carbon atom separates the two parts of each water molecule. Glucose is one of the simplest.

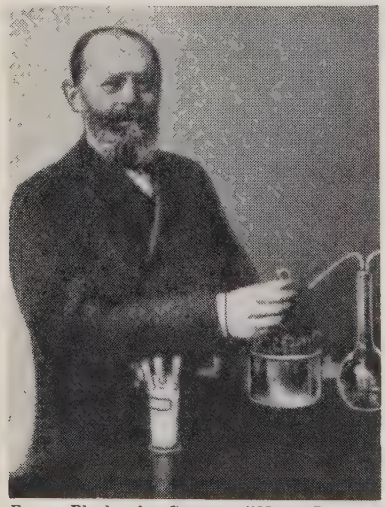


The carbohydrates are mostly of vegetable origin and include such complex materials as starch and cellulose as well as the sugars. The more complex ones are built up from simple units such as glucose. A molecule of water is removed when each pair of simple units unite to form a larger unit. Water will hydrolyze the larger units into smaller units. Such hydrolysis does not yield an acid and a base like the hydrolysis of a salt.

2. Glucose and fructose. The most important simple sugars are *glucose* and *fructose*. These sugars are hexoses and have the general formula, $C_6H_{12}O_6$. Glucose is in corn syrup and is often known as *dextrose*. It is found in honey,

in many fruit juices and in grapes, whence it is sometimes known as *grape sugar*. It is produced by the hydrolysis of more complex sugars and starches. The hydrolysis of cane sugar produces glucose and its isomer fructose.

Glucose is the main fuel used by living cells. Without fire or flame it is oxidized in the tissues along with fats and amino acids at just the right rate to supply the energy needed by the body in the process known as metabolism. This oxidation proceeds to carbon dioxide and water when the body is healthy and normal. Since glucose is ready to burn in the cells without digestion it is used in infant feeding formulas and for injection into the veins for immediate nourishment. The utilization of glucose in the cells is controlled by a hormone secreted by the pancreas and known as *insulin*. When glucose is not properly assimilated by the cells the oxidation of other foods does not proceed normally. This



From Black & Conant: "New Practical Chemistry", courtesy The Macmillan Company.

Fig. 238. Emil Fischer (1852-1919), a German organic chemist, studied the carbohydrates and the proteins.

Fig. 239. Sir Frederick Banting (1891-1941), Canadian chemist, received the Nobel Prize for his discovery of insulin.

disease is known as *diabetes*. The insulin treatment of diabetes was discovered and developed by the late Sir Frederick Banting, Dr. Best and Dr. Collip in the Connaught Laboratories in Toronto. The unused glucose is eliminated in the urine and its presence may be determined by *Fehling's solution*. This reagent consists of two solutions, one of cupric sulphate, and the other of sodium hydroxide and rochelle salts. The two solutions are mixed together before use. If a solution containing glucose is added and the mixture heated, the cupric hydroxide will be reduced and a red precipitate of cuprous oxide will be obtained. From its reaction with this reagent, glucose is known as a *reducing sugar*.

3. **Sucrose,** $C_{12}H_{22}O_{11}$, or *cane sugar* is the most familiar sugar. It is obtained from sugar cane or sugar beets, but it is present in the sap of many trees and in the juices of several fruits. The sugar obtained from sugar cane and sugar beet is identical with that in maple sugar or syrup, the taste and odour of maple products being due to other substances. In the preparation of sugar, the canes or beets are sliced and pressed to obtain the juice. This juice is evaporated under reduced pressure to prevent decomposition and charring, and a crude sugar is obtained. This crude sugar is taken to refineries where it is dissolved in water and filtered through beds of charcoal to remove the colouring matter. Carbon dioxide is passed through the solution to precipitate calcium salts, which may then be removed by filtration. The colourless syrup is evaporated in vacuum pans until crystals commence to form. The crystals are removed and centrifuged to dry them and provide *granulated sugar*. The mother liquor from which the crystals are obtained at various stages of the process furnishes *molasses*. The sugar which reaches our tables is almost 100 per cent pure, and is the purest chemical compound used by man. Lump sugar is made by pressing moist granulated sugar into the required form and allowing

it to dry. If sucrose is allowed to crystallize slowly, large monoclinic crystals known as rock candy are produced.

Sucrose melts at about 185°C. and decomposes partially at about 220°C. to produce a brown substance known as *caramel*, which is used as a colouring and flavouring material in many food products. As we have seen, sucrose hydrolyzes in the presence of a dilute acid to give glucose and fructose.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose is monoclinic and it does not reduce Fehling's solution. The mixture of glucose and fructose produced by the hydrolysis of sucrose is known as *invert sugar* and the process is called *inversion*. Invert sugar reduces Fehling's solution. It does not crystallize as does sucrose, and for this reason it is used in the manufacture of confectionery, where crystallization would be undesirable. Honey consists largely of invert sugar as the sucrose which is gathered by the bee is inverted by formic acid or enzymes in the insect's body before being deposited in the comb. Invert sugar is not as sweet as sucrose. It is used as a moistening agent with tobacco products to prevent them from becoming too dry during storage. If yeast is added to a solution of sucrose, the yeast cells produce an enzyme called *invertase* which causes the production of invert sugar. Another enzyme, called *zymase*, acts upon the glucose and fructose to produce ethyl alcohol and carbon dioxide.

4. Maltose and lactose. *Maltose* is produced from starch by the action of an enzyme called *diastase* which is found in the seed germ. When barley and other grains germinate their starch is converted to maltose by this enzyme, and if the germinated grain is heated and dried, a product known as *malt* is obtained. Malt contains diastase and will cause the hydrolysis of starch, producing

a mixture of maltose and dextrin. Dextrin consists of many sugar molecules.

$$(C_6H_{10}O_5)_x + H_2O \longrightarrow \underset{\text{maltose}}{C_{12}H_{22}O_{11}} + \underset{\text{dextrin}}{(C_6H_{10}O_5)_{x-2}}$$

The addition of yeast will cause an enzyme-promoted hydrolysis which converts the maltose into glucose and, finally, the yeast converts the glucose into ethyl alcohol. Maltose and lactose are isomers of sucrose. For this reason they all have the same formula $C_{12}H_{22}O_{11}$. Maltose is a reducing sugar, and yields only glucose when hydrolyzed.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 2\ C_6H_{12}O_6$$

During digestion in the body this hydrolysis is brought about by the enzyme *amylopsin*. The conversion of starch into maltose is commenced by the *ptyalin* in the saliva, and the production of glucose is completed in the intestine. Maltose is a good food since one molecule produces two molecules of glucose which is assimilated readily.

Lactose or *milk sugar* is found in cow's milk to the extent of about 5 per cent. It is not as sweet as sucrose and is not as soluble in water. In the preparation of ice cream, lactose may crystallize at low temperatures because of its small solubility and will thus produce a displeasing granular texture. The addition of gelatin, which acts as a protective colloid, prevents this condition.

Lactose is a reducing sugar and hydrolyzes to form glucose and galactose. Milk turns sour because of the production of lactic acid during the fermentation of lactose, which is caused by the action of bacteria present in the air.

$$\underset{\text{lactose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow 4\ \underset{\text{lactic acid}}{CH_3CHOHCOOH}$$

If the milk is kept at a temperature of about 65°C. for about an hour, the bacteria in the milk will be killed and the milk will not become sour. This process is known as *pasteurization*

and is employed to kill harmful bacteria that may be present in the milk.

5. Starch and *cellulose* are complex carbohydrates with the general formula, $(C_6H_{10}O_5)x$, where x is a whole number whose value cannot be determined. Starch is stored in grains, tubers and fruits as a source of food for the young plant. It occurs in small granules which exhibit different sizes, shapes and other characteristics, depending on their source. Because of these different properties, starch from various sources is used for different purposes. Rice starch is used for face powder and for finishing cotton cloth. Arrowroot starch is used for food and laundry work. Wheat starch has marked adhesive properties and is used for the manufacture of paste. When starch is heated with water the granules swell and their cellulose covering bursts. The starch then forms a gelatinous mass, and on longer heating, a small amount will dissolve in the water. Prolonged treatment with hydrochloric acid produces a variety known as *soluble* starch, which will dissolve in water, and is familiar in laboratory work. Because the bursting of the granules by heat liberates the starch, the starch of cooked foods is attacked more readily by digestive fluids than that from raw foods. At temperatures around 200°C. starch is changed into dextrin which is used in making brown gravy. It chars at a higher temperature. Starch does not reduce Fehling's

From Black & Conant: "New Practical Chemistry", courtesy The Macmillan Company.

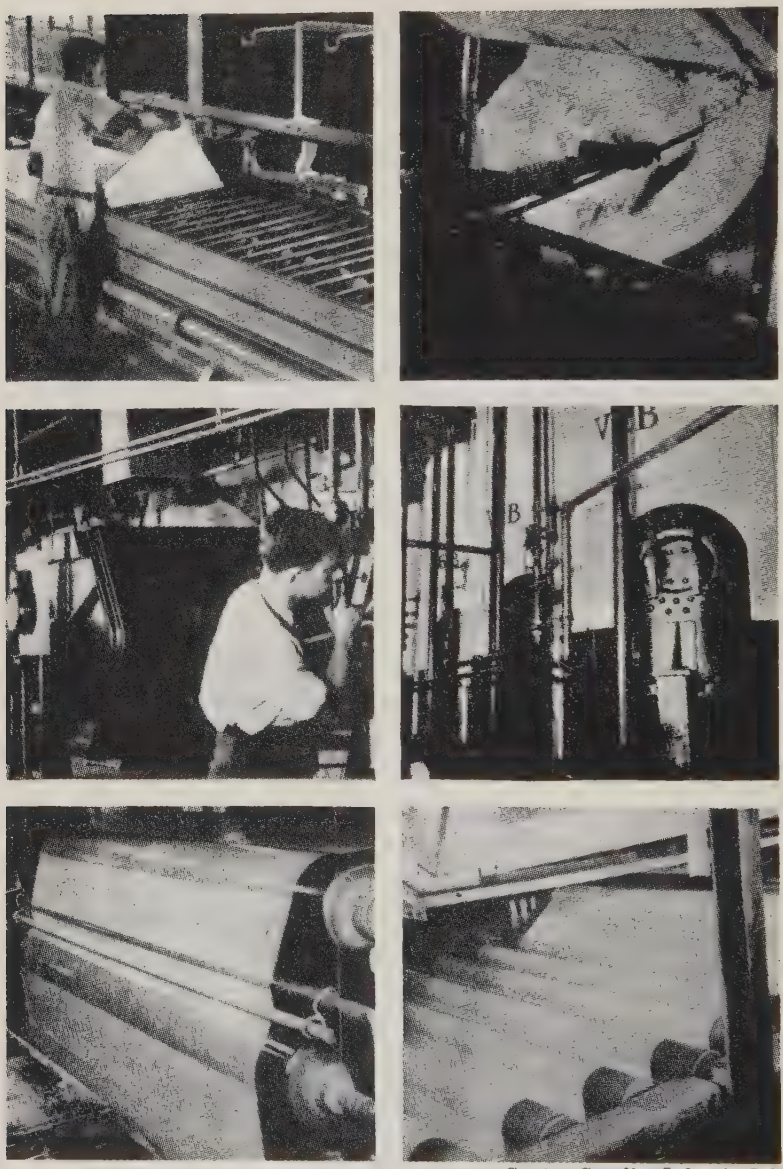
Fig. 240. Starch granules differ in shape in different plants.

solution, but it hydrolyzes readily with acids and enzymes such as ptyalin from saliva, producing dextrin, maltose and glucose. The final product of hydrolysis in the body is glucose. Starch gives a characteristic blue colour with iodine that is used as a test for either iodine or starch.

6. Cellulose has the same empirical formula as starch, but its structure and its molecular weight are not known. It forms the woody portion of all plants, in which it appears as longitudinal cells bound together by lignin. It is a suitable constituent for the walls of plant cells because it is a comparatively stable substance insoluble in simple solvents. Cotton wool is comparatively pure cellulose, while washed filter paper is almost entirely pure cellulose.

The moderate action of nitric acid in the presence of sulphuric acid produces *cellulose nitrate* or *pyroxylin*. This substance is soluble in a mixture of alcohol and ether and the solution is known as *collodion*. Pyroxylin is used in the manufacture of lacquers, photographic film, artificial leather, and celluloid. Lacquers use the pyroxylin dissolved in a solvent such as amyl acetate. Artificial leathers are made by impregnating canvas cloth with solutions of cellulose nitrate. Celluloid is prepared by mixing pyroxylin, camphor and alcohol, and pressing the mass into blocks at high temperatures. The material becomes hard on cooling and may be cut into sheets as desired. A more complete nitration of cellulose produces *gun cotton*. This is used in the manufacture of explosives, such as smokeless powder, cordite and dynamite.

Natural cotton fibres are flat, twisted and shrivelled. If cotton cloth is treated with a solution of sodium hydroxide, the cellulose becomes partially hydrated and the fibres swell and straighten. This process is known as *mercerization*, and cotton treated in this manner has a softer and smoother texture than untreated cotton. If pure cellulose sheets are treated with dilute sulphuric acid and then washed and dried,



Courtesy Canadian Industries Ltd.

Fig. 241. Some of the processes used in the manufacture of Cellophane.

parchment paper is produced. This paper is tough and somewhat translucent.

Cellulose acetate is made by treating cellulose with acetic acid, acetic anhydride and a catalyst. It is similar to cellulose nitrate, but it is not explosive and is not so combustible. Safety photographic film is made from cellulose acetate. If cellulose acetate is dissolved in an organic solvent and the solution forced through small openings into a large chamber, the solvent will evaporate, leaving the acetate in the form of threads. These threads may be made into a silk-like cloth known as *celanese*.

Cellulose from wood pulp may be treated with sodium hydroxide and carbon disulphide to form *cellulose xanthate*. When this substance is treated with sodium hydroxide it forms *viscose*, which is held in solution. If this solution is forced through small openings into a bath which regenerates the cellulose, threads are formed which may be woven into the fabric known as *rayon*. If the viscose is forced through a narrow slit a thin sheet known as *cellophane* is produced.

(See Fig. 241 on opposite page).

Upper left: The sulphite pulp is steeped in lye.

Upper right: The alkali cellulose is shredded into fibres.

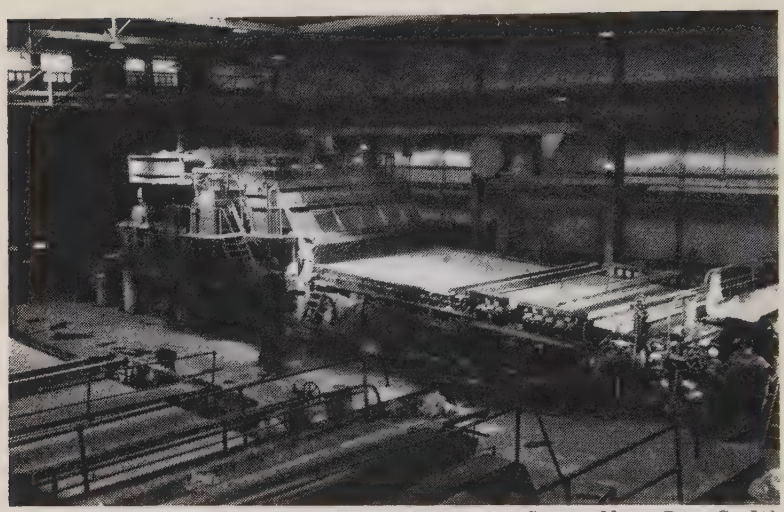
Middle left: Churned with carbon disulphide it is converted into cellulose xanthate.

Middle right: The xanthate is mixed with lye, filtered and ripened in tanks.

Lower left: Forced through a slit into an acid bath, it forms a film.

Lower right: The sheet is washed, bleached, dried and rolled.

7. Paper. Early paper was made entirely from rags, and even now many high grades of paper are made from them. Most cheap paper is made from the cellulose obtained from wood. Logs for the paper mill are cut into lengths of about four feet, and, when so cut, are known as *pulp wood*. Canada is one of the largest producers of pulp wood. This wood may be ground off by huge grindstones to make ground-



Courtesy Mersey Paper Co. Ltd.

Fig. 242. The wet end of a paper-making machine.

wood pulp. The pulp wood may also be chipped and treated chemically to dissolve the lignin which holds the cellulose fibres together. There are several methods of doing this, but a solution of calcium bisulphite is usually used, the wood chips being soaked at an elevated temperature until the lignin is dissolved. The material is then known as *sulphite pulp.* Various proportions of sulphite and the cheaper groundwood pulp are blended, washed with water and bleached with sulphur dioxide. The effect of this bleaching wears away with age and old paper frequently becomes yellow. The pulp is now made into paper in one of the longest machines used in industry. One end of this machine is known as the *wet end* and the other, the *dry end.* At the wet end, the washed and bleached pulp is allowed to flow onto a travelling wire screen through which the surplus water drains away, leaving a matte of pulp on the screen. The cellulose fibres become meshed together, so that after a while they form a wet thick sheet of paper which can be picked off the screen and carried

along through rollers. These rollers squeeze out the excess water and further the drying process. During this process one roller may carry a raised design which is impressed on the paper and forms the *watermark* appearing in the finished sheet as an indentifying trademark. The paper finally passes through heated rollers and a complete roll of paper is obtained at the dry end of the machine.

A small amount of paper is produced by hand. The pulp, which is made from fine-quality rags, is shaken on screens until the water drains away, and it is then dried in presses. In the manufacture of paper, many substances are added to the pulp to produce different types of paper. Starch, glue, rosin, and similar materials, are added to act as *sizing*, so that the paper may be resistant to soaking up ink. Barium sulphate is added frequently as a filler to produce the heavy shiny paper used in illustrated books and magazines. Pigments may be added as well. The waste materials of the paper industry contain large quantities of lignin, which, at the present time, has few uses. No doubt some day you will see this waste material as the source of many synthetic substances.

8. Photosynthesis. Perhaps the most intriguing synthesis in the world is that performed by the green plant in sunlight. The waste products of combustion and oxidation, carbon dioxide and water, are used to reform the sugars and then the starches and celluloses. From these the plant and animal organisms are able to fashion the multitudinous compounds and structures which make up living things. The equation is simple to write:

$$6\ CO_2 + 6\ H_2O \longrightarrow C_6H_{12}O_6 + 6\ O_2$$

We know this is a photochemical reaction where the radiant energy of sunlight is converted into chemical energy by means of a complex organic compound called *chlorophyll*.

It is thought that formaldehyde may be first formed and its molecules might then unite to form the simple sugars which in turn unite to give the more complex ones. Oxygen is produced at the same time.

$$(1) \quad H_2O + CO_2 \longrightarrow H.CHO + O_2$$
$$(2) \quad 6\ H.CHO \longrightarrow C_6H_{12}O_6$$

Man has not been able to achieve such a synthesis in his laboratories and the exact mechanism remains a greater mystery than the structure of the nucleus of an atom.

These processes in the plant are thus the reverse of the fundamental processes of hydrolysis and oxidation which furnish the energy for life. The various celluloses and sugars are hydrolyzed to simple sugars by the processes of digestion and the simple sugars are then oxidized to carbon dioxide and water by the same amount of oxygen used in their production.

9. Proteins. Perhaps the most wonderful food of man consists of complex organic substances containing nitrogen which are known as *proteins*. Familiar examples are the *albumin* of eggs, the *casein* of milk, the *gluten* of flour, and the *hemoglobin* of blood.

All proteins contain carbon, hydrogen and oxygen in addition to nitrogen, and some of them may contain sulphur and phosphorus. The exact chemical composition of these substances has not been determined, and their molecular weight must be very large. When proteins decompose they yield *amino acids*, which contain the amino radical ($-NH_2$). Some actual proteins have been known to yield more than twenty *different* amino acids on decomposition.

During digestion of food, the proteins are hydrolyzed by the digestive fluids of the stomach, which contain the enzyme *pepsin*, and are converted into *peptones* and *proteoses*. In the small intestine several enzymes, one of them being

trypsin, convert the proteins into amino acids, which are passed into the blood where they are converted into *serum albumin* by enzyme reaction. Serum albumin is used to build the complex proteins found in the body and an excess is changed into carbohydrates and fats. Worn-out tissue converts proteins or serum albumin to urea which is eliminated in the urine.

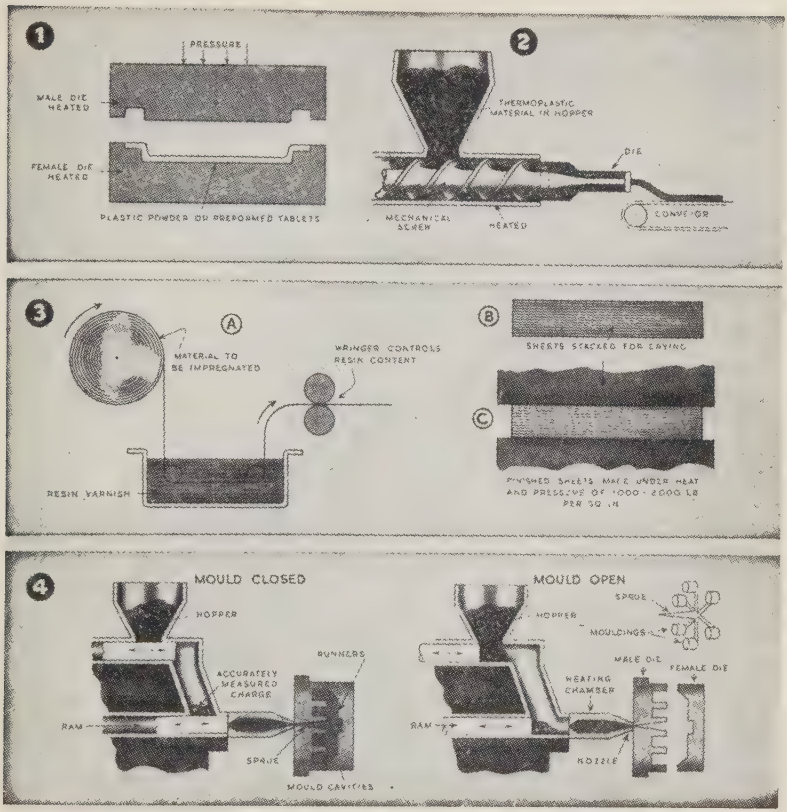
10. Complete organic materials. We have traced the story of matter from the understanding of the simplest chemical changes to the molecular structure of fats and simple carbohydrates. The detailed structure of naturally occurring organic materials is still largely undiscovered but we already understand a good deal about the general arrangement of organic units in eggs, milk, vegetables, silk, hair, hides, glue, wood, and even flesh itself. Some of these characteristics have already been discussed but two other factors should be mentioned. One of these is *polymerization* or the joining of molecules with one another to form long chains. The other process is *cross-linkage* or the union of groups on molecules with other groups on neighbouring molecules to form a web or a mesh of inter-connected atomic chains. When molecules of water are split off during the combination of molecules or reactive groups the processes are often referred to as *condensations*. The complex structures of nature and our synthetic resins, plastics and textiles are formed by the processes of polymerization and cross-linkage. Nature also adds the feature of structural organization to her products. We know more about the complex materials which we create synthetically than we do about natural products so we will mention plastics first.

The term "plastic" may be applied generally to any substance which may be formed by the application of heat or pressure, or both, and can retain its form afterwards. Glass, pitch and tar are considered as plastics, but the term is now

applied to synthetic resins. Resins were formerly obtained from vegetable sources. *Rosin* is produced from pine oil as a by-product of the turpentine industry, and *amber* is a fossil resin.

The ancestor of modern plastics is celluloid which was made from cellulose nitrate by Hyatt in 1869. Lacquers made from cellulose nitrate and acetate were introduced around 1920. The first synthetic resin was *bakelite* which was prepared by the condensation of formaldehyde and phenol by Baekland in 1907. Phenol is carbolic acid or hydroxybenzene and when it is heated with formaldehyde in the presence of a little acid or alkali the solution thickens. When the condensation is carried out in the presence of an acid catalyst, it produces a resinous substance that can be softened by heat and is soluble in certain solvents. This material can be used as a lacquer because it becomes hard when the solvent evaporates. Paper and cloth can be impregnated with the solution of the resin, and will become hard when treated with steam. These impregnated articles can be built up in layers, and the laminated material used to make small gears and other parts for machinery. Many substances, such as wood pulp, can be used as fillers and the material pressed into moulds. If the condensation is carried out in the presence of a base, with additional formaldehyde and increased temperature, a hard material is obtained. This substance is insoluble in almost all solvents and does not soften with increased temperature. Objects made from bakelite are hard and durable, and are good insulators of electricity. It may be said that the use of plastics has revolutionized the electrical industry. Bakelite is used for pipe stems, fountain pens and pencils, automobile accessories, gears, and the insulating portion of electrical equipment.

In addition to bakelite, there are now a large number of plastic materials for which new uses are being found every



Courtesy Canadian Industries Ltd.

Fig. 243. Processes used in the fabrication of plastic articles.
1. Compression moulding uses heat and pressure.
2. Extrusion moulding produces continuous rods, tubes or strips.
3. Lamination binds paper, cloth, wood or metal into sheets.
4. Injection moulding forms small parts like casting does.

day. These plastics are *thermoplastic resins* or *thermosetting resins*. A thermoplastic resin is one which will become soft when heated and will remain in that condition until it is allowed to cool. It may thus be melted and run into moulds where it will become hardened on cooling. A thermosetting resin will become soft when heated but will become hard when held at the high temperature. When it becomes hard it is permanently insoluble and infusible.

Urea-formaldehyde resins produce a transparent material which is tougher than glass but much softer. It can be used to make articles that are to be lighter in colour than those which are made from bakelite. It is used for cups and dishes, ash trays, etc.

The *acrylate* resins are made by the polymerization of methyl acrylate. They are clear and colourless, and can be moulded and worked with tools. They can be used for lenses and prisms in optical instruments. There are many of these resins, one of the better known ones being *Lucite*, which has the interesting property of transmitting light throughout its length. A rod of Lucite will transmit light as if it were flowing through a pipe, even though the rod be bent at right angles. This property is made use of for certain types of surgical instruments, where a light must shine around a corner.

Nylon is produced by the condensation of substances known as hexamethylenediamine and adipic acid to produce a substance which is somewhat like a protein in its composition. The melted material is forced through small openings to form threads. The solidified threads are woven into cloth which resembles silk, but is said to be more durable and more elastic. It is used to make hosiery, brush bristles, racquet strings, and insulation for electrical equipment. During World War II it was used to make parachutes and tow rope for glider aircraft and had many other important uses.

The *vinyl* resins are prepared by the polymerization or condensation of *vinyl chloride*, *vinyl acetate* and *vinylidene chloride*. These resins are mostly thermoplastic and some of them are used because of their adhesive properties in cartons, plywood and safety glass. They are often made in the form of thin sheets, and have been used for hospital sheeting, life rafts, water bags and flexible pipes. *Koroseal* is used for water-proof curtains. Some of this material has considerable

tensile strength. The vinyl compounds can be made from acetylene so they are produced at Shawinigan Falls.

Proteins and cellulose are the chief chemical substances in natural materials. They are mostly organized into living cells and the material used by man is the cell walls or the whole cell. Eggs are the stored material for the formation of the tiny chicken. From the albumin in the egg white the proteins are built. The mineral salts contain calcium and phosphorus to construct the bones and the yolk contains the stored starches and fats to supply the energy. Eggs are thus a complete food for body building.

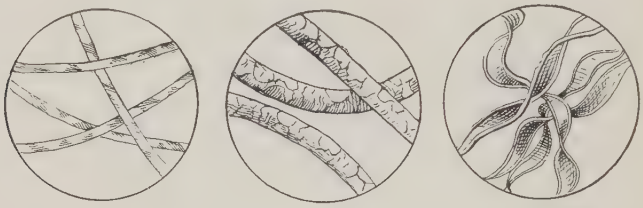
Milk is another complete food containing proteins in the form of *casein* and *lactalbumin*, and fats and sugar in the form of lactose. The necessary minerals and vitamins are also present.

The vegetables are composed of cells where cellulose makes the cell walls and proteins make the fluid material in the cells. Wheat contains *gluten* as the chief protein, while peas and beans contain *legumin*. Wood is constructed like the vegetables but the cellulose is bound together by a substance known as *lignin*. Hardly any of the vegetable proteins contain all of the 22 "essential" amino acids needed by the body to construct its tissues. The proteins found in the buckwheat and the velvet bean are the only complete proteins with all the necessary amino acids.

Certain proteins found in fresh lean meat contain all the essential amino acids but meat contains little carbohydrate. One of the most abundant proteins in meat is called *myosin*. The oxidation of proteins in the body for energy throws a heavy load on the elimination systems so a balanced diet is recommended.

Besides the natural materials used as food large quantities are used as textiles. A textile material should have very long narrow fibres to give it flexibility and strength. Silk and

wool are animal fibres which are largely proteins. Wool also contains sulphur in addition to carbon, hydrogen, oxygen and nitrogen. The plant fibres such as cotton, jute, hemp and sisal are nearly pure cellulose.



From Black & Conant: "New Practical Chemistry", courtesy The Macmillan Company.

Fig. 244. Textile fibres differ in their microscopic appearance.

The animal and vegetable fibres differ in their microscopic appearance. The experienced microscopist can tell cotton fibres by their flat and twisted appearance, wool by its scales and the cylindrical smooth linen fibres by their taper. The scales on wool and the twisted cotton fibres hold together well during spinning and all synthetic fibres seek to duplicate their behaviour.

The animal fibres can be distinguished from the vegetable fibres because they are protein in nature. For example:

(1) Hot 5% sodium hydroxide destroys silk and wool.

(2) Cold concentrated hydrochloric acid destroys cotton and linen but it attacks silk only slowly; wool is resistant to its action.

(3) Nitric acid stains animal proteins a yellow colour which turns to orange in the presence of ammonia. Alkalis and oxidizing agents weaken and destroy wool and silk fabrics so laundry soaps containing free alkali or chlorine bleaches should never be used for washing such articles. Wool fibres become brittle in a hot place because high heat hardens proteins, so they should be woven or dried at moderate temperatures.

What has been said of wool applies to the other fine animal hairs used in textiles. *Mohair* is the fleece of the Angora goat, *cashmere* that of the Tibetan goat and *fur felt* is made from rabbit hair.

Hides are mainly protein in nature. There is a thin outer layer, the epidermis, which carries the hair in a small depression called the hair follicle. The temperature control mechanisms, the sweat glands, also have their outlets in the epidermis so it is known as the thermostat layer. Its tissues are made of a protein known as *keratin*. The remaining part of the skin known as the derma or corium is made of *collagen*, a very strong, long-fibred protein said to be made up of 288 amino acid groups attached end to end. About thirteen different amino acids have been found in collagen. In the making of leather the collagen is rendered insoluble in water by treatment with sodium dichromate or tannin.

Before the skin is tanned it is soluble in hot water and the resulting solution is called *gelatin*. If the gelatin is heated longer in the water it jells less readily but is more sticky so it is called *glue*. Tannins are orange-coloured materials which can be extracted from bark and they precipitate glue or gelatin and make collagens insoluble and resistant to decay.

11. Minerals and vitamins. In addition to the fats, carbohydrates and proteins mentioned previously, the human diet should contain small quantities of other substances, whose presence is necessary for the maintenance of health. These substances are the *body minerals* and the *vitamins*. In every ordinary well balanced diet, there should be plenty of minerals and vitamins, but in the case of infants using prepared foods, and adults living on an extremely unbalanced diet, the food supply may be insufficient in regard to these important substances. The minerals needed by the body are usually supplied by foods and water. In order of their

abundance in the human body they are calcium, phosphorus, potassium, sulphur, sodium, chlorine, magnesium, iron, iodine, fluorine and traces of other elements. These elements form bones and teeth, which are mainly inorganic calcium phosphate, and in addition they form parts of organic molecules. It is thought that many are more readily assimilated by the body when they are combined by plants or animals into proteins and other organic substances.

In addition to the pure nutrients—proteins, carbohydrates and fats—plus the proper minerals, the body requires small amounts of organic substances which facilitate the healthy utilization of food. These substances are called vitamins because they appear to be necessary for life. They prevent the deficiency diseases such as scurvy, rickets and beriberi.

12. The continuing search. Although the inquisitive mind has progressed a long way from the superstitions of primitive man we have still a great deal to learn about the nature and uses of matter.

(*i*) The complex materials are still to be taken apart and put together again before they are thoroughly understood.

(*ii*) The causes and cures for a multitude of human diseases are as yet little known but a major effort is being made to conquer cancer and other diseases.

(*iii*) We are only entering the plastic age and a whole host of new synthetic fibres and materials of all kinds can be developed for a thousand purposes.

(*iv*) We will learn to find new sources of oil in coal and oil shales or we will develop new types of fuel or energy.

(*v*) New and improved alloys of the metals can be discovered and the inroads of corrosion and wear reduced.

(*vi*) Our vast industrial wastes such as sawdust, lignin and tailings, may be turned to use in building and in providing new sources of chemicals.

(*vii*) The secret of such natural processes as photosynthesis may be unearthed and the whole field of synthetic food production opened up.

(*viii*) The energy of the nucleus may be used to perform hitherto impossible tasks such as the diversion of the Labrador current, the removal of mountains, ice fields and other natural obstacles.

With peace, activity and intelligence, the story of matter can have many new instalments.

Question Summary

1. What are carbohydrates? What is their origin?
2. (*a*) Describe glucose and its function in the body.
   (*b*) What is the use and action of Fehling's solution?
3. (*a*) Describe the production of sucrose.
   (*b*) Describe the properties of sucrose and the production of invert sugar.
4. (*a*) Describe maltose and lactose.
   (*b*) What is dextrimaltose? Why is it and maltose a good food?
   (*c*) Why is the pasteurization of milk required in cities?
5. Where does starch occur in nature? What are its properties? What is a test for starch?
6. (*a*) Where does cellulose occur and what are its properties?
   (*b*) Describe the action of nitirc acid on cellulose and describe the products that are formed.
   (*c*) Describe the production of cellulose acetate products.
   (*d*) Describe the production of viscose products.
7. (*a*) Describe the production of paper.
   (*b*) What materials are sometimes added to pulp during the manufacture of paper?
8. Why is photosynthesis such a remarkable chemical reaction?
9. (*a*) What are proteins? Give some examples.
   (*b*) Discuss the composition of proteins.
   (*c*) Describe briefly the digestion of proteins.
10. (*a*) Describe the processes involved in forming complex materials.
    (*b*) What are plastics? What are natural resins?
    (*c*) How was the first plastic made?
    (*d*) Describe bakelite.
    (*e*) Describe some of the more modern plastics.

(*f*) What are the peculiar properties of Lucite?
(*g*) Describe the production of nylon.
(*h*) Describe the vinyl resins.
(*i*) What is the general structure of natural fibres?
(*j*) Why are milk and eggs regarded as complete foods?
(*k*) Why can wool and silk be detected in the presence of cotton?
(*l*) How are glue, gelatin and hides related?

11. What minerals are required by the body?

12. Discuss some of the unsolved problems about matter.

Appendix

READABLE READING

BAWDEN, *Man's Physical Universe*, The Macmillan Company, New York, 1943 (or The Macmillan Company of Canada Limited, Toronto).

COITH, *So You Want To Be A Chemist*, McGraw-Hill Book Co., New York, 1943 (or McGraw-Hill Co., of Canada Ltd., Toronto).

CURIE, EVE, *Madame Curie*, Garden City Publishing Co., Inc., New York, 1940 (or Blue Ribbon Books, Toronto).

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LANDIS, *Your Servant the Molecule*, The Macmillan Company, New York, 1944 (or The Macmillan Company of Canada Limited, Toronto).

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WARRINGTON AND NICHOLLS, *A History of Chemistry in Canada*, Published for The Chemical Institute of Canada by Sir Isaac Pitman & Sons, Toronto, 1949.

Many interesting articles on individual subjects will be found in current periodicals such as:

Journal of Chemical Education, 20th & Northampton St., Easton, Pa.

Life, 530 So. Michigan Ave., Chicago, Ill.

Scientific American, 24 West 40th St., New York.

Canadian Chemistry and Process Industries, Westman Publications, 263 Adelaide St. W., Toronto, Canada.

INDUSTRIAL INFORMATION AND VISUAL AIDS

Much useful and interesting information about Canadian chemical activities may be obtained from the companies listed below. Wherever necessary the chief subjects dealt with are shown in brackets. There are a great many other companies in Canada, the United States, Great Britain and elsewhere who can supply films and literature about their manufacturing processes. Those listed are known to supply both films and literature.

Aluminum Company of Canada Limited, 1700 Sun Life Bldg., Montreal, P.Q.
Anaconda American Brass, Ltd., New Toronto, Ont. (Copper).
Atlas Steels Limited, Welland, Ont. (Tool and Alloy Steels).
Bakelite Company (Canada) Limited, 163 Dufferin St., Toronto 1, Ont.

Arnold Banfield and Company Limited, Oakville, Ont. (Plastics).
Calco Chemical Division, North Cyanamid Ltd., Toronto 1, Ont. (Dyes).
Canadian Carborundum Co., Ltd., Niagara Falls, Ont. (Grinding).
Canadian Cottons Ltd., 760 Victoria Square, Montreal, P.Q. (Blankets).
Canadian General Electric Co., Ltd., Toronto, Ont. (X-rays etc.).
Canadian Industries Limited, P.O. Box 10, Montreal, P.Q. (Fabrics, Fertilizers, Salt, Insecticides, Dyes, Rubber, Drugs, etc.).
Canadian Johns-Manville Company, 199 Bay St., Toronto, Ont. (Insulation etc.).
Canadian National Carbon Company, 805 Davenport Road, Toronto 4, Ont.
Howard Smith Paper Mills Ltd., 407 McGill Street, Montreal, P.Q.
Imperial Oil Limited, 56 Church Street, Toronto, Ont.
The International Nickel Company of Canada Limited, Toronto 1, Ont.
The Upjohn Co., 384 Adelaide Street West, Toronto, Ont. (Vitamin B).

Additional educational films can be obtained through the various provincial departments of education and through the regional film libraries of the National Film Society. The addresses of local agents and regional offices as well as descriptive lists of the films available may be obtained from the following:

Associated Screen News, 1330 Sherbrooke St. West, Montreal, Que.
Eastman Kodak Co., Teaching Films Division, Toronto, Ont.
General Films Limited, 156 King St. W., Toronto 1, Ont.
J. Arthur Rank Movies Ltd., 431 Yonge St., Toronto, Ontario.
The National Film Society of Canada, 172 Wellington St., Ottawa.

The Chemical Institute of Canada, 18 Rideau St., Ottawa, has an excellent descriptive list of the various films on chemical and allied subjects.

TABLES FOR REFERENCE

Atomic Weights	Last page of book
Density of Gases at S.T.P.	Chap. 7, Sec. 9
Electrochemical or Activity Series	Chap. 38, Sec. 6
Flame Tests	Chap. 38, Sec. 7
Metric Units of Length and Weight	Chap. 3, Sec. 4
Periodic Table	Chap. 30, Sec. 6
Solubility of Compounds	Chap. 38, Sec. 5
Specific Gravity of Some Common Elements	Chap. 3, Sec. 4
Tests for Ions	Chap. 38, Sec. 7
Valences of Elements	Chap. 10, Sec. 6
Vapour Pressure of Water	Chap. 15, Sec. 5

COMMON NAMES OF SUBSTANCES

Common Name	Chemical Name	Formula
Alum	Potassium aluminum sulphate	$K_2SO_4.Al_2(SO_4)_3.24H_2O$
Baking soda	Sodium bicarbonate	$NaHCO_3$
Borax	Sodium tetraborate	$Na_2B_4O_7.10H_2O$
Calomel	Mercurous chloride	Hg_2Cl_2
Caustic potash	Potassium hydroxide	KOH
Caustic soda	Sodium hydroxide	$NaOH$
Chalk (precipitated)	Calcium carbonate	$CaCO_3$
Corrosive sublimate	Mercuric chloride	$HgCl_2$
Cream of tartar	Potassium hydrogen tartrate	$KHC_4H_4O_6$
Epsom salts	Magnesium sulphate	$MgSO_4.7H_2O$
Gypsum	Calcium sulphate	$CaSO_4.2H_2O$
Hypo	Sodium thiosulphate	$Na_2S_2O_3.5H_2O$
Lime (quicklime)	Calcium oxide	CaO
Limestone or marble	Calcium carbonate	$CaCO_3$
Limewater	Calcium hydroxide solution	$Ca(OH)_2$
Moth balls	Naphthalene	$C_{10}H_8$
Plaster of paris	Calcium sulphate hemihydrate	$(CaSO_4)_2.H_2O$
Putty	Calcium carbonate in linseed oil	
Red lead (minium)	Double lead oxide	Pb_3O_4
Sal ammoniac	Ammonium chloride	NH_4Cl
Sugar	Sucrose	$C_{12}H_{22}O_{11}$
Vinegar	Dilute acetic acid	$HC_2H_3O_2$
Washing soda	Sodium carbonate	$Na_2CO_3.10H_2O$

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TABLE OF INTERNATIONAL ATOMIC WEIGHTS

Element	*Symbol*	*At. No.*	*At. Wt.*	*Element*	*Symbol*	*At. No.*	*At. Wt.*
Actinium	Ac	89	227 *ca.*	Mercury	Hg	80	200.61
Alabamine	Ab	85	221 *ca.*	Molybdenum	Mo	42	95.95
Aluminum	Al	13	26.97	Neodymium	Nd	60	144.27
Americium	Am	95	..	Neon	Ne	10	20.183
Antimony	Sb	51	121.76	Neptunium	Np	93	239 *ca.*
Argon	A	18	39.944	Nickel	Ni	28	58.69
Arsenic	As	33	74.91	Nitrogen	N	7	14.008
Barium	Ba	56	137.36	Osmium	Os	76	190.2
Beryllium	Be	4	9.02	Oxygen	O	8	16.0000
Bismuth	Bi	83	209.00	Palladium	Pd	46	106.7
Boron	B	5	10.82	Phosphorus	P	15	30.98
Bromine	Br	35	79.916	Platinum	Pt	78	195.23
Cadmium	Cd	48	112.41	Plutonium	Pu	94	239 *ca.*
Calcium	Ca	20	40.08	Polonium	Po	84	210 *ca.*
Carbon	C	6	12.01	Potassium	K	19	39.096
Cerium	Ce	58	140.13	Praseodymium	Pr	59	140.92
Cesium	Cs	55	132.91	Protactinium	Pa	91	231
Chlorine	Cl	17	35.457	Radium	Ra	88	226.05
Chromium	Cr	24	52.01	Radon	Rn	86	222
Cobalt	Co	27	58.94	Rhenium	Re	75	186.31
Columbium	Cb	41	92.91	Rhodium	Rh	45	102.91
Copper	Cu	29	63.54	Rubidium	Rb	37	85.48
Curium	Cm	96	..	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.000	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.066
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Illinium	Il	61	146 *ca.*	Thorium	Th	90	232.12
Indium	In	49	114.76	Thulium	Tm	69	169.4
Iodine	I	53	126.92	Tin	Sn	50	118.70
Iridium	Ir	77	193.1	Titanium	Ti	22	47.90
Iron	Fe	26	55.85	Tungsten	W	74	183.92
Krypton	Kr	36	83.7	Uranium	U	92	238.07
Lanthanum	La	57	138.92	Vanadium	V	23	50.95
Lead	Pb	82	207.21	Virginium	Vi	87	224 *ca.*
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Masurium	Ma	43		Zirconium	Zr	40	91.22

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